



# UNIT 15 CHEMICAL EQUILIBRIUM

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## STUDY GUIDE

This Unit consists of three components: the text, two experiments and a TV programme. The two experiments are integrated with the text, one in Section 2, and one in Section 4.2. In both cases, the manipulations are very simple and each experiment should take about 40 minutes. The best results are obtained by using distilled or deionized water, which can be bought from any good chemist or garage. One litre should be adequate.

The TV programme, 'Equilibrium rules—OK?', supports Sections 4 and 5, and you will gain most benefit from it if you have studied up to the end of Section 4.5 before viewing the programme. Notes on the programme are in Section 8.

You will also be able to use a computer-assisted learning (CALCHEM) program via the terminal at your local Study Centre. This program provides exercises and examples related to Sections 4 and 5.

### I INTRODUCTION

Let us begin this Unit with a thought experiment, using the elements hydrogen, chlorine and iodine which you met in Units 13–14.

At room temperature, hydrogen and chlorine are gases that consist of diatomic molecules. Suppose we mix 1.2 moles of  $H_2(g)$  and 1.0 mole of  $Cl_2(g)$  in a glass bulb at room temperature. The colourless hydrogen and yellow-green chlorine react to form another colourless gas, hydrogen chloride:



Eventually the reaction stops, and there is no further change. Suppose we now find out what the bulb contains.

- What substances would you expect to find, and in what amounts?
- According to Equation 1, the 1.0 mole of  $Cl_2$  will react with 1.0 mole of  $H_2$  to give 2.0 moles of  $HCl(g)$ . Apart from this  $HCl$ , there should just be 0.2 mole of unchanged  $H_2$ . *No chlorine should be present.*

This answer is correct, but it is made possible by an assumption. We have assumed that Reaction 1 is complete: that it proceeds until, *as far as we can detect*, one of the reactants has been completely used up. You made the same assumption about the tin–iodine reaction in Experiment 2 of Units 13–14. In many cases this assumption is very satisfactory, but we shall now look at an instance where it is not.

Suppose we repeat the hydrogen–chlorine experiment with 1.2 moles of  $H_2$  and 1.0 mole of  $I_2$ . Iodine is a solid at room temperature, so to make both the reactants gaseous, as they were before, we will heat the bulb to, say, 427°C. At this temperature, iodine is a purple vapour. The purple colour fades as the iodine reacts with the hydrogen to form the colourless gas, hydrogen iodide:



This time however, the reaction stops before all the iodine colour has faded, and no matter how long we wait, it will not disappear. At this point, the bulb contains about 0.35 mole of  $H_2$ , 0.15 mole of  $I_2$  and 1.70 moles of  $HI$ .

In this case, therefore, the reaction does not go to completion; measurement shows that, when the reaction is over, all the substances on both the left-hand and right-hand sides of Equation 2 are detectable. In such cases, we say that there is a state of balance, or *chemical equilibrium*, between the two sides of the equation, between the reactant(s) and the product(s).

If chemical equilibrium decides the extent of a chemical reaction, chemists and the chemical industry need to be thoroughly acquainted with it. In

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ACID

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BASE

---

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INDICATOR

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Units 15 and 16, we explore the nature of chemical equilibrium using illustrative examples. For two reasons, our examples will mainly involve the reactions of ions in aqueous solution: first, such reactions can often be performed with simple chemicals and glassware; secondly, they are often fairly quick, dramatic and important. From this Unit for instance, you can work out why orange juice is more palatable than vinegar, and why power stations increase the acidity of rainwater. However, before you can tackle either chemical equilibrium, or these questions, you must first consolidate and extend what you already know about aqueous ions, and this is the purpose of Sections 2 and 3.

In Experiment 4 of Units 13–14, you classified aqueous solutions by their electrical conductivity. Now we shall classify them by studying their effect on a substance called litmus. This is a dye extracted from the lichen lichen (*Roccella tinctoria*), which grows on cliffs along the coasts of the Canary Islands, and southern and western Europe. Surprisingly enough, we shall then find that the two kinds of classification can be related.

## 2 ACIDS AND BASES (Experiment 1)

Today, chemists are wary of the chemicals that they work with, but in the Middle Ages they were made of sterner stuff. For example, during that time, chemists noticed that the solutions of some substances possessed a sour taste whereas others tasted bitter and felt greasy when they were rubbed between finger and thumb. The first type of substance (or its solution) they called an **acid** (Latin, *acidus*, sour), and the second has come to be known as a **base**. A later and more complete classification of acids and bases is given below.

The aqueous solution of an acid:

has a sour taste;

is capable of changing the colour of many naturally occurring dyes. For example, it turns syrup of violets and many other blue vegetable substances red;

in many cases, dissolves chalk to produce a gas. Chalk is calcium carbonate ( $\text{CaCO}_3$ ) and the gas liberated when it is dissolved in an acid is carbon dioxide ( $\text{CO}_2$ );

in many cases, dissolves metals such as magnesium or zinc to produce hydrogen gas ( $\text{H}_2$ ).

The aqueous solution of a base:

has a bitter taste;

feels greasy;

is capable of restoring the colour of many naturally occurring dyes after they have been changed by an acid.

In Experiment 1 we ask you to classify a number of chemical and household substances simply by testing their action on the dye litmus. DO NOT TASTE THEM! Dyes whose colours respond to the action of acids and bases are called **indicators**.

# EXPERIMENT 1

## CLASSIFICATION OF SOME CHEMICAL SUBSTANCES IN SOLUTION ACCORDING TO THEIR ACTION ON LITMUS

**TIME**

about 40 minutes

**NON-KIT ITEMS**

distilled water

**KIT ITEMS**

*Chemical tray*  
 ammonia solution ( $2\text{ mol l}^{-1}$ )  
 dilute acetic acid ( $2\text{ mol l}^{-1}$ )  
 dilute hydrochloric acid ( $2.4\text{ mol l}^{-1}$ )

litmus papers, blue and red  
 litmus, solid  
 magnesium hydroxide  
 sodium carbonate  
 sodium chloride  
 sodium hydroxide

*Tray A*  
 dropping pipette  
 test-tubes (nine)  
 glass stirring rod

*Tray C*  
 measuring spoon (spatula-type)  
 spatula  
 test-tube brush  
 test-tube rack  
 wash bottle

*Part 1*

This part of the experiment is concerned with four solids, magnesium hydroxide, sodium hydroxide, sodium chloride and sodium carbonate. Add one of the solids to a clean, dry test-tube until the rounded bottom is just about full. (*Use too little rather than too much.*) Label the test-tube with the name of the solid. Now repeat this operation with the other three solids and three more test-tubes. Add distilled water from the wash bottle to a depth of 2 cm to the four test-tubes and shake to mix. Now tear up a red and a blue litmus paper into small pieces and add one red and one blue piece to each test-tube. If both papers become red, call the substance an acid; if both become blue, call it a base. If neither paper changes colour, classify the substance as 'neutral'. Put ticks in the appropriate columns of Table 1, which has already been completed for some other common substances. *Please remove the papers from the  $\text{Mg(OH)}_2$  test-tube with the glass rod and retain the test-tube and contents for future work in Section 4.*

TABLE 1 Classification of some chemical and household substances in aqueous solution according to their action on litmus

Solute	Acid	Base	Neutral
<b>SOLIDS</b>			
calcium hydroxide			✓
magnesium hydroxide			
sodium chloride			
sodium carbonate			
sodium hydroxide			
potassium nitrate			
sugar			
washing soda			✓
<b>LIQUIDS</b>			
ammonia ( $2\text{ mol l}^{-1}$ )			
acetic acid ( $2\text{ mol l}^{-1}$ )			
hydrochloric acid ( $2\text{ mol l}^{-1}$ )			
vinegar	✓		
lemon juice	✓		
orange juice		✓	
washing-up liquid		✓	
the 'air' you breathe out (containing carbon dioxide, $\text{CO}_2$ )			✓

*Part 2*

This part of the experiment is concerned with the ammonia, acetic acid and hydrochloric acid solutions. Add two or three drops of your ammonia solution to about a 2 cm depth of distilled water in a fresh, clean test-tube. Test with litmus paper as in Part 1. Rinse the pipette with distilled water, and repeat this test with acetic acid instead of ammonia solution; then repeat with hydrochloric acid. Again put ticks in Table 1.

*Part 3*

Litmus also comes in a solid soluble form. Make up a solution of it by dissolving half a 'spoonful' in a 4 cm depth of distilled water. *Again, do not exceed this amount.* Divide the solution in two and blow through one part with a washed dropping pipette (a drinking straw will do equally as well). You may need to do this for up to five minutes to get

## EXPERIMENT CONTINUED

a perceptible result. Does the part you blow through become more red or more blue when compared with the other solution that you prepared? Record your conclusion in Table 1.

### Part 4

If you wish, you can check the entries for common household substances in Table 1 that we have completed for you by mixing the substances with distilled water.

Now clean your glassware with water, retaining just the  $\text{Mg}(\text{OH})_2$  test-tube as advised. You may wish to keep the glassware and chemicals to hand, since several of the items will be needed for Experiment 2.

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### NEUTRALIZATION

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### ARRHENIUS DEFINITIONS

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The classification of Table 1 is consistent with household experience. Thus, like lemon juice and many other citrus fruit juices, vinegar tastes sour. As you probably know, vinegar is essentially a dilute aqueous solution of acetic acid, and the citrus fruits contain citric acid. Among the bases, you are probably familiar with the slippery feel of washing soda and soap solution, and with the unpleasantly bitter taste of the latter.

## 2.1 NEUTRALIZATION

Section 2 defined distinct, characteristic properties of acids and bases, but it did not explain why the two kinds of substance should be discussed under the same heading. One very good reason is their capacity for mutual destruction, a process which is called **neutralization**. Consider sodium hydroxide solution and hydrochloric acid. If they are mixed in the right amounts, the bitter taste of the base and the sour taste of the acid disappear, the mixture no longer changes the colour of litmus paper, and it tastes rather like seawater. The distinctive properties of an acid or a base disappear when one is added to the other. This type of reaction is called a neutralization reaction. Thus, in addition to its characteristic properties listed in Section 2, an acid reacts with a base to destroy or diminish its basic properties. Likewise, a base reacts with an acid to destroy or diminish its acidic properties.

## 2.2 INFLUENCE OF THE IONIC THEORY ON THE CONCEPTS 'ACID' AND 'BASE'

So far, the terms 'acid' and 'base' have been defined by the external effects that they have on other objects or materials (including each other, and ourselves!). This type of definition is said to be *operational*: it merely lists the operations that define the class of compounds. But these definitions provide no chemical reason why an acid or base possesses the characteristic properties that it does. Let us try to redeem this failing.

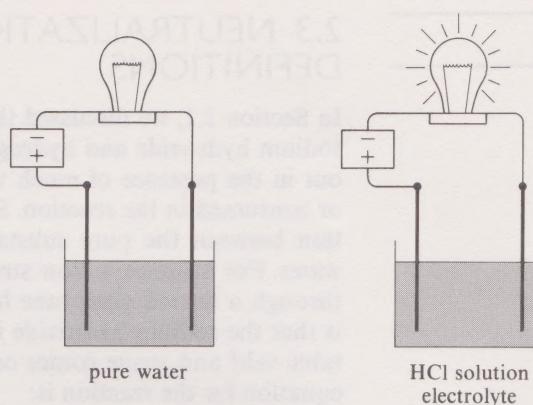
The hydrochloric acid that you used in Experiment 1 is made by dissolving gaseous hydrogen chloride ( $\text{HCl}$ ) in water. If this solution is tested with the equipment used in Experiment 4 of Units 13–14 (Figure 1), the bulb lights up. Thus in water,  $\text{HCl}$  breaks down into ions, and in Section 7.6 of Units 13–14, we wrote the breakdown as:



Two other very well-known acids are nitric and sulphuric acids. They have the formulae  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , respectively, and their aqueous solutions also conduct electricity.

## THE ARRHENIUS DEFINITION OF ACIDS AND BASES

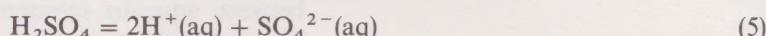
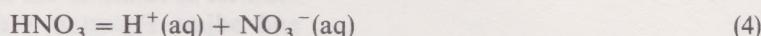
When 5 cm<sup>3</sup> of dilute hydrochloric acid are added to 50 cm<sup>3</sup> of water and tested as in Experiment 4 of Units 13–14, the bulb lights up. HCl is an electrolyte: its aqueous solution contains ions.



(3)  $\text{H}_2\text{O} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{HCl}$

no aqueous except salt and water  
salt solution salt to water, because no  
water except a few  
electrolytes more to neutralise  
only make solution salt and salt  
should expand but different  
hence all water except  
water

- Write possible dissociation reactions for  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  in water.
- Among the common aqueous ions listed in Table 5 of Units 13–14 are  $\text{H}^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . Thus plausible dissociation reactions are:



- Look at Equations 3, 4 and 5. What do aqueous solutions of HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  have in common?
- They contain a common ion,  $\text{H}^+(\text{aq})$ .

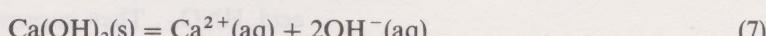
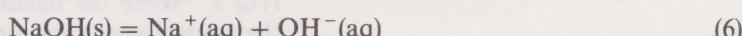
Perhaps therefore, the common acidic properties of the three solutions are caused by the presence of  $\text{H}^+(\text{aq})$ . If so, then *an acid can be defined as a substance that yields hydrogen ions,  $\text{H}^+(\text{aq})$ , in aqueous solution*. Try ITQ 1 to convince yourself that this definition accounts for two of the characteristic properties of an acid.

**ITQ 1** From Table 5 of Units 13–14,  $\text{Mg}^{2+}(\text{aq})$  and  $\text{Ca}^{2+}(\text{aq})$  are the ions that Mg and Ca are likely to form in aqueous solution. If an acid is simply a substance that yields  $\text{H}^+(\text{aq})$  ions in aqueous solution, write balanced equations that represent:

- (a) the reaction between magnesium metal, Mg, and an aqueous acid, in which  $\text{H}_2$  gas is evolved;
- (b) the reaction between calcium carbonate,  $\text{CaCO}_3$ , and an aqueous acid, in which  $\text{CO}_2$  gas and water are formed.

Now let us turn to bases. Consider two of these, sodium hydroxide,  $\text{NaOH}$ , and calcium hydroxide,  $\text{Ca}(\text{OH})_2$ : when dissolved in water, both form conducting solutions.

- Write equations for what happens when the two substances dissolve.
- Among the aqueous ions listed in Table 5 of Units 13–14 are  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{OH}^-$ . Thus plausible dissociation reactions are:



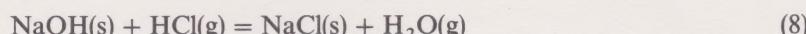
- Can you now suggest a new definition of a base?
- According to Equations 6 and 7, it seems likely that *a base is a substance that yields hydroxide ions,  $\text{OH}^-(\text{aq})$ , in aqueous solution*.

These definitions of an acid and a base were first proposed in 1887 by the Swedish chemist, Svante Arrhenius, as part of his ionic theory for electrolyte solutions. They are known as the **Arrhenius definitions**, and they allow an elegant interpretation of the simple neutralization reactions discussed in Section 2.1.

## SALT

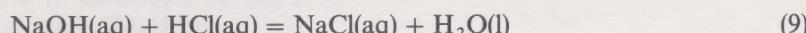
## 2.3 NEUTRALIZATION AND THE ARRHENIUS DEFINITIONS

In Section 2.1, we discussed the reaction between *aqueous solutions* of solid sodium hydroxide and hydrogen chloride gas. When the reaction is carried out in the presence of much water, one cannot detect if water is produced or consumed in the reaction. Suppose, however, that we carry out this reaction between the pure substances without bothering to dissolve them in water. For instance, a slow stream of hydrogen chloride gas could be passed through a heated glass tube full of solid sodium hydroxide. What happens is that the sodium hydroxide is turned into solid sodium chloride (ordinary table salt) and *steam* comes out of the other end of the tube. The balanced equation for the reaction is:

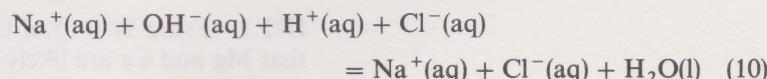


Thus by using the pure substances rather than the aqueous solutions, we see clearly that water molecules are an actual *product* of the reaction. This is not easily detected when the reaction happens in aqueous solution.

Now let us return to the reaction in aqueous solution at room temperature, and adjust Equation 8 accordingly. This time the reaction takes place between aqueous solutions of sodium hydroxide and hydrogen chloride. The products are sodium chloride and condensed steam (water). We could therefore write the reaction:



- What criticism can be made of Equation 9?
- In aqueous solution, NaOH, HCl, and NaCl consist of aqueous ions. This is not revealed by Equation 9.
- Rewrite the equation so as to rectify this.
- A reasonable answer is



However, this can be improved. The best kind of chemical equation gives us the *bare essentials of the chemical changes that occur*. In Equation 10, the ion  $\text{Na}^+(\text{aq})$  appears on both sides of the equation. This means that it is not changed by the reaction. Thus if it is eliminated from each side, the equation will still remain balanced, and still correctly describe the chemical change that has occurred.

- Rewrite Equation 10 by eliminating the ions that occur on both sides.
- By eliminating  $\text{Na}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$ , we get



This result is very much simpler.

**ITQ 2** Write the balanced equation that corresponds to Equation 10 for the neutralization reaction between potassium hydroxide, KOH, and nitric acid,  $\text{HNO}_3$ . Then improve the equation by eliminating the ions that occur on both sides.

ITQ 2 should have driven home the point that Equation 11 describes all simple neutralization reactions in water. The characteristic properties of an acid in aqueous solution are due to the presence of  $\text{H}^+(\text{aq})$  ions, whereas those of a base are caused by  $\text{OH}^-(\text{aq})$  ions. In neutralization reactions where acidic and basic properties suffer mutual annihilation, the  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  ions combine to form water. Notice that this is one reason why acids and bases are important in many natural systems: they are linked through one of our vital compounds, water!

Equation 11 is a very elegant and general way of describing what happens in neutralization reactions. However, the alternative equation, Equation 9, does have one advantage: it tells us what solid substance we will get if, after the reaction has occurred, the products are dried out by evaporation of the water.

What is this solid substance?

■ Sodium chloride. The products in Equation 9 are water and an aqueous solution of sodium chloride: this explains the salty taste of the solution mentioned in Section 2.1. Loss of water leaves the solid.\*

The overall result is that the base (sodium hydroxide) reacts with an acid (hydrochloric acid) to give water, which evaporates, and salt (sodium chloride), which contains the cation of the base and the anion of the acid. Because this reaction is the standard example of a large class of neutralization reactions, the word **salt** is now used as a general name for the solid residue left behind after the reaction between any acid and any base. Such neutralization reactions can be generally written as



In such an equation the ‘salt’ is an ionic compound in which the cation, the positive ion, is derived from the base, and the anion, the negative ion, from the acid. Equations 11 and 12 are alternative ways of expressing the general reaction between a base and an acid in water. Equation 12 is helpful in identifying products, but it is Equation 11 that captures the essence of what happens.

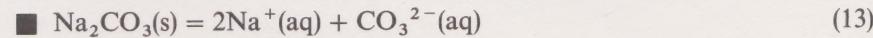
**ITQ 3** The solution produced by the reaction between KOH and HNO<sub>3</sub> in ITQ 2 is warmed so that the water evaporates. Name the solid residue, give its chemical formula, and state to what class of compounds it belongs.

## 2.4 THE ARRHENIUS DEFINITIONS: SOME LOOSE ENDS

Bases such as NaOH, Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> clearly contain the hydrogen and oxygen needed for the hydroxide ions that they form when they dissolve in water. Likewise, acids such as HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> contain the hydrogen needed for the formation of hydrogen ions. However, in Table 1, you should have found that solutions of ammonia (NH<sub>3</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) were bases, and that a solution of CO<sub>2</sub> was slightly acidic. Yet NH<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> do not contain the required OH combination, and CO<sub>2</sub> lacks hydrogen. Can the Arrhenius definitions survive these discrepancies?

The answer is that they can, if we allow the solvent water molecules to participate in the equation that leads to the formation of H<sup>+</sup>(aq) or OH<sup>-</sup>(aq). For example, consider sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>.

Write an equation for what happens when this solid dissolves in water.

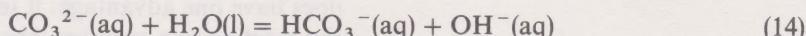


So far, no OH<sup>-</sup>(aq) has appeared. However, in Table 5 of Units 13–14, we identified the bicarbonate ion, HCO<sub>3</sub><sup>-</sup>, as a common anion in aqueous solution. When sodium carbonate dissolves in water, a small proportion of

\* If you would like to try this experiment, first make up a solution of litmus as in Part 3 of Experiment 1. Dissolve two pellets of sodium hydroxide in about a 3 cm depth of water in a test-tube. Add two or three drops of your litmus solution, and then add dilute hydrochloric acid, drop by drop from a dropping pipette, shaking the solution as you do it, until the litmus just turns red. Pour the resulting solution into a saucer and leave it in a warm place. Inspect it when it has dried out.

## CONCENTRATION

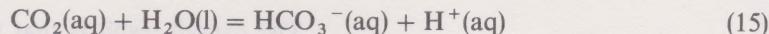
the  $\text{CO}_3^{2-}(\text{aq})$  on the right-hand side of Equation 13 reacts with water to form  $\text{HCO}_3^-(\text{aq})$ :



In the process some  $\text{OH}^-(\text{aq})$  is formed, and this accounts for the basic properties of the solution.

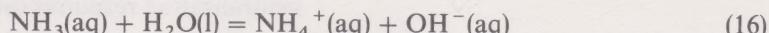
Write a similar equation that shows how dissolved  $\text{CO}_2$ ,  $\text{CO}_2(\text{aq})$ , can act as an acid.

Again a little of the  $\text{CO}_2$  forms  $\text{HCO}_3^-(\text{aq})$ :



Now try to write an equation that shows how dissolved ammonia,  $\text{NH}_3(\text{aq})$ , can act as a base

Table 5 of Units 13–14 lists the ammonium ion,  $\text{NH}_4^+$ , as a common cation in aqueous solution. We write



This reaction does indeed occur, although only to a limited extent: most dissolved ammonia remains as  $\text{NH}_3(\text{aq})$ .

Thus by invoking Reactions 14, 15 and 16, which we emphasize occur only to a limited extent, the Arrhenius definitions can survive the three apparent exceptions.

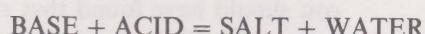
## SUMMARY OF SECTION 2

1 The aqueous solution of a typical acid tastes sour, turns blue litmus red, and dissolves magnesium, chalk and zinc. These characteristic properties are eliminated by the addition of a base.

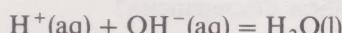
2 The aqueous solution of a typical base tastes bitter, feels greasy and turns red litmus blue. These characteristic properties are eliminated by the addition of an acid.

3 These properties are explained by the Arrhenius definitions: acids yield  $\text{H}^+(\text{aq})$  in aqueous solution; bases yield  $\text{OH}^-(\text{aq})$  in aqueous solution.

4 The typical acid–base neutralization reaction can be written as



where the salt is a combination of the cation of the base with the anion of the acid. However, a more elegant description is



**SAQ 1** Tick to show which and how many of the words (a)–(d) refer to the statements (i)–(v).

	(a) an acid	(b) a base	(c) a salt	(d) water
(i) A substance that gives curdled milk its sour taste.				
(ii) A substance that is formed in the reaction between aqueous solutions of an acid and a base.				
(iii) A substance that turns red litmus blue				
(iv) A substance that gives soap its slippery feel				
(v) A substance that reacts with zinc to give hydrogen gas				

**SAQ 2** Write balanced equations of the type shown in Equation 10 for the neutralization reactions between: (i) aqueous solutions of calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , and nitric acid,  $\text{HNO}_3$ ; (ii) aqueous solutions of lithium hydroxide,  $\text{LiOH}$ , and sulphuric acid,  $\text{H}_2\text{SO}_4$ .

Eliminate unchanged aqueous ions from both equations and show that they then reduce to Equation 11.

**SAQ 3** Name and give the chemical formulae of the solids obtained by evaporating to dryness the solutions produced by the reactions in SAQ 2.

**SAQ 4** Magnesium oxide,  $\text{MgO}$ , and sulphur trioxide,  $\text{SO}_3$ , are both solids. When added to water,  $\text{MgO}$  acts as a base, and  $\text{SO}_3$  acts as an acid. Write balanced equations that show that this is consistent with the Arrhenius definitions. Table 5 of Units 13–14 may help you in selecting likely products.

### 3 THE CONCENTRATION OF A SOLUTION

Before you can study chemical equilibrium, you must understand one property of solutions that can be measured and expressed in numbers and units. Imagine two glasses of water. Suppose we dissolve one domestic sugar lump in one glass and two lumps in the other. The resulting solutions of sugar in water are different: the second is more *concentrated* than the first.

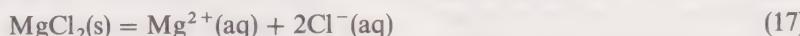
A useful way of describing such differences is to state the **concentration** of each solution. Concentrations can be specified in various ways. For instance, we could state the mass of dissolved sugar in a particular volume of solution.

**ITQ 4** Suppose that each domestic sugar lump has a mass of 5 g, and that when the single sugar lump has dissolved in our first glass of water, the volume of the solution in the glass is  $200 \text{ cm}^3$ . What is the concentration of such a solution in grams of sugar per litre of solution ( $\text{g l}^{-1}$ )? (Remember 1 litre =  $1000 \text{ cm}^3$ )

Specifying the mass of solute in a litre of solution is a perfectly valid way of expressing concentrations. However, as you saw in Units 13–14, chemical reactions are most conveniently thought of as reactions between small whole numbers of *moles* of substances. In chemistry, therefore, it is more useful to express concentrations as the number of *moles* of solute in one litre of solution (this is sometimes called the molarity of the solution).

**ITQ 5** The chemical name of domestic sugar is sucrose, and it has the rather complex chemical formula  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . What is the concentration of the solution of ITQ 4 in moles of sucrose per litre of solution ( $\text{mol l}^{-1}$ )? Use the relative atomic masses: C = 12; H = 1; O = 16.

The concentrations of solutions of ionic substances can also be expressed in this way, but in such cases something extra must be borne in mind. Suppose that 0.02 mole of magnesium chloride ( $\text{MgCl}_2$ ) is dissolved in enough water to make one litre of solution. Obviously the concentration is  $0.02 \text{ mol l}^{-1}$ . However, from Section 6.3 of Units 13–14, you know that  $\text{MgCl}_2$  dissociates in water:



We can state the concentration of the solution as 0.02 mole of  $\text{MgCl}_2$  per litre because of the way the solution has been made. But we must remember that the dissolved  $\text{MgCl}_2$  is present as  $\text{Mg}^{2+}(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  ions.

- In one litre of the solution, how many moles of  $\text{Mg}^{2+}(\text{aq})$  ions and how many moles of  $\text{Cl}^-(\text{aq})$  ions are present?

**SATURATED SOLUTION****SOLUBILITY****CHEMICAL EQUILIBRIUM**

■ According to Equation 17, every mole of  $MgCl_2$  that dissolves yields 1 mole of  $Mg^{2+}(aq)$  and 2 moles of  $Cl^-(aq)$ . Thus the 0.02 mole of dissolved  $MgCl_2$  in one litre of solution is present as 0.02 mole of  $Mg^{2+}(aq)$  and 0.04 mole of  $Cl^-(aq)$ .

We could therefore describe the solution of  $MgCl_2$  by saying that it contains  $0.02\text{ mol l}^{-1}$  of  $Mg^{2+}(aq)$  and  $0.04\text{ mol l}^{-1}$  of  $Cl^-(aq)$ . However, it is customary to use the more concise description, which is derived from the way the solution was made, and to say that we are dealing with a solution of  $MgCl_2$  of concentration  $0.02\text{ mol l}^{-1}$ .

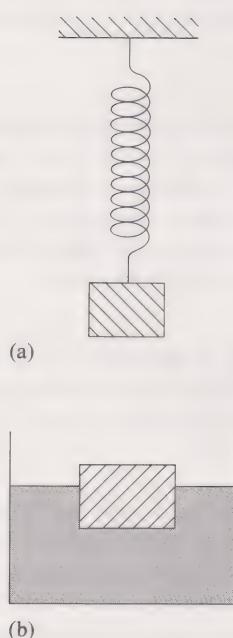
**SAQ 5**  $500\text{ cm}^3$  of a solution of sodium sulphate contains 7.1 g of dissolved  $Na_2SO_4$ . Calculate the concentration of (i) the solution, in  $\text{mol l}^{-1}$  of  $Na_2SO_4$ ; (ii)  $Na^+(aq)$  in  $\text{mol l}^{-1}$ ; (iii)  $SO_4^{2-}(aq)$  in  $\text{mol l}^{-1}$ . Use the approximate relative atomic masses: Na = 23; S = 32; O = 16.

## SUMMARY OF SECTION 3

The amount of a chemical substance dissolved in a given volume of a solution is known as the concentration of that substance in the solution. Concentrations are usually expressed in moles per litre.

## 4 CHEMICAL EQUILIBRIUM

You are now ready to pursue the concept of chemical equilibrium, which was introduced in Section 1. To those who have not made an academic study of the term, the word ‘equilibrium’ implies a state of balance characterized by the appearance of quiescence: nothing seems to change as time passes. Such equilibrium is typified by a motionless object suspended from a spring (Figure 2a): this is a case of *mechanical equilibrium*. Another familiar example is the case of *hydrostatic equilibrium* shown in Figure 2b: a motionless block of wood floating in stagnant water. When we discuss chemical equilibrium, we shall occasionally pause, and compare it with such systems. As you will see, there are important similarities, and also important differences between chemical equilibrium and the other sorts. But first, we must consider a fresh example of chemical equilibrium through which the comparison can conveniently be made.



**FIGURE 2** Two everyday instances of equilibrium: (a) a motionless object suspended from a spring—a case of mechanical equilibrium; (b) a block of wood floating in water—a case of hydrostatic equilibrium. Both examples have the appearance of quiescence: nothing seems to change with time.

### 4.1 A SATURATED SOLUTION: AN EXAMPLE OF CHEMICAL EQUILIBRIUM

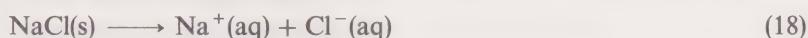
A small amount of salt will dissolve easily in a cup of water. Add a little more, and that will dissolve as well. But this process cannot go on indefinitely: sooner or later, solid salt collects at the bottom of the cup, and no matter how hard you stir, or how long you wait (provided the temperature remains constant) no more will dissolve.

Can you suggest why we insist that the temperature stays constant?

■ The temperature is a factor that determines how much substance dissolves. Most solids, including sugar and salt, become more soluble in water as the temperature rises.

When, at a particular temperature, we reach the point when no more solute will dissolve in a solvent, the solution is said to be **saturated** at that temperature. The concentration of the solute in the saturated solution is then called the **solubility** of the solute in the solvent. For a particular combination of solute and solvent at a particular temperature, the solubility is a constant. For example, at  $25^\circ\text{C}$  a saturated solution of sodium chloride in water contains  $359.0\text{ g l}^{-1}$ .

Suppose we add a large amount of salt to some water at 25 °C and stir. To begin with, the solid dissolves to form aqueous sodium and chloride ions:



In this equation, we have emphasized the direction of the dissolving process by replacing the usual equals sign with an arrow drawn from the reactant (solid NaCl) to the products (the aqueous ions). As more salt dissolves, the concentration of the solution rises and eventually reaches 359.0 g l<sup>-1</sup>. At this point, the solution is saturated, and no more solid will dissolve. From then on, provided the temperature remains constant, the mass of solid salt at the bottom of the container, and the concentration of the solution above it, do not change with time. The system has ‘the appearance of quiescence’ referred to in Section 4, and the solid salt is said to be in **chemical equilibrium** with its saturated solution.

To summarize, the dissolving process, which in this case is represented by Equation 18, is limited: it can only go as far as the position of equilibrium allows. That position of equilibrium corresponds to the coexistence of undissolved solid with a saturated solution.

## 4.2 CHEMICAL EQUILIBRIUM—A STATE OF DYNAMIC BALANCE (Experiment 2)

You should have retained another example of a saturated solution from Experiment 1. This is a test-tube containing a suspension of solid magnesium hydroxide, Mg(OH)<sub>2</sub>, in water.

When you made it up, you could not possibly have detected any dissolving of solid just by looking at it. This is because very little magnesium hydroxide dissolves—we say that magnesium hydroxide is very sparingly soluble in water. Nevertheless, there is some dissolution, and you subsequently found evidence for it.

- What evidence was this?
- In Experiment 1, you showed that the solution in contact with the solid turned red litmus paper blue. This suggests that some of the magnesium hydroxide has dissolved and produced aqueous hydroxide ions. The dissolution reaction is like that of Ca(OH)<sub>2</sub> in Equation 7:



Obviously the solubility of magnesium hydroxide in water is much less than that of sodium chloride. At 25 °C, one litre of the saturated solution contains only 0.011 g of dissolved solid. Nevertheless, your test-tube is still an example of chemical equilibrium akin to the sodium chloride case discussed in Section 4.1. It contains solid magnesium hydroxide in equilibrium with aqueous magnesium and hydroxide ions.

Take a look at the test-tube. All should seem quiet. Given that the temperature is constant, neither the mass of the white solid, nor the concentration of the solution above it, is changing. The dissolving reaction, Equation 19, has apparently stopped. But this calm is deceptive. If you could climb into a frogman’s outfit, shrink to the size of a water molecule and swim about in the test-tube, things would look very different. There is an experiment which can demonstrate this.

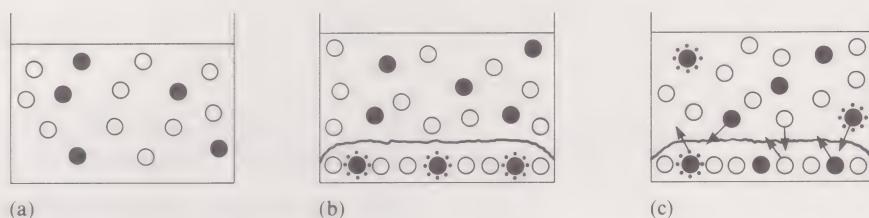
Many of the chemical elements around us are a blend of isotopes. This was demonstrated in Section 2.2.2 of Units 11–12. For example, the naturally occurring magnesium in your sample of Mg(OH)<sub>2</sub> consists of the isotopes <sup>24</sup>Mg, <sup>25</sup>Mg and <sup>26</sup>Mg. However, by using a nuclear reactor, it is possible to make magnesium hydroxide containing the isotope <sup>28</sup>Mg, and this

isotope is radioactive. Chemically, this radioactive hydroxide behaves just like ordinary  $\text{Mg}(\text{OH})_2$ , but the radioactive magnesium in it can be detected with a suitable device, such as a geiger counter.

Now suppose we add some of this solid  $^{28}\text{Mg}(\text{OH})_2$  to your test-tube. Once this solid has been added, there seems again to be no change: the amount of solid magnesium hydroxide does not diminish and the concentration of the saturated solution does not increase. This is what we would expect:  $^{28}\text{Mg}(\text{OH})_2$  behaves chemically just like natural  $\text{Mg}(\text{OH})_2$ , and so the equilibrium is not disturbed. But if after a time, we filter off the solid, the residual solution is found to be radioactive due to the presence of  $^{28}\text{Mg}^{2+}(\text{aq})$ . Now, following the addition of  $^{28}\text{Mg}(\text{OH})_2(\text{s})$ , there has been no increase in the total concentration of dissolved magnesium hydroxide.

- So how can the presence of  $^{28}\text{Mg}^{2+}(\text{aq})$  in the solution be explained?
- Some  $^{28}\text{Mg}(\text{OH})_2(\text{s})$  must have dissolved, but this has been exactly balanced by the counter-movement of other isotopes of magnesium from the solution into the solid (Figure 3).

**FIGURE 3** Radioactive labelling reveals the dynamic equilibrium that exists between a solid and its saturated solution. (a) A saturated solution of magnesium hydroxide: filled circles represent  $\text{Mg}^{2+}(\text{aq})$ ; open circles  $\text{OH}^-(\text{aq})$ , the ratio being 1 : 2. (b) The same immediately after the addition of  $^{28}\text{Mg}(\text{OH})_2$ : radioactive magnesium is represented by a halo of dots. (c) After some time: the concentration of the saturation solution is the same even though  $^{28}\text{Mg}$  has moved into the solution because there is a counter-movement of non-radioactive magnesium into the solid.



At equilibrium, therefore, the reaction



proceeds just as it did before equilibrium was reached. The reverse reaction



however is also proceeding at an equal rate, and there is no net transfer of magnesium hydroxide in either direction. Beneath the apparent quiescence of the equilibrium state, there is, at the level of ions and molecules, a ceaseless coming and going. Chemical equilibrium is a *dynamic* process in which the forward (left → right) and reverse (right → left) reactions are going on at equal rates. To represent this, we shall write equilibrium systems with two half-headed arrows pointing in opposite directions. Thus a saturated solution of magnesium hydroxide is represented by the equation



Notice that although the hydrostatic equilibrium in Figure 2b resembles chemical equilibrium in its quiescence, it does not have this dynamic quality. This is a property where the analogy between the two systems breaks down.

You should now do Experiment 2. It consists of three parts, and provides practical demonstrations of the theoretical discussion still to come. Part 1 drives home the two-directional quality of Equilibrium 21 in a fresh way; the results are discussed in Section 4.3. Parts 2 and 3 illustrate the way in which the position of chemical equilibrium can be dramatically shifted by adding certain other chemicals. Part 2 works on Equilibrium 21, and the results are discussed in Section 4.4. Part 3 works on a new example of chemical equilibrium which will be of major concern throughout the rest of the Unit.

Record the results of the Experiment in your Notebook. You will need to refer to them later.

## EXPERIMENT 2

### CHEMICAL EQUILIBRIUM AND LE CHATELIER'S PRINCIPLE

**TIME**

about 40 minutes

**NON-KIT ITEMS**

distilled water  
clean dry saucers (three)

**KIT ITEMS**

*Chemical tray*  
dilute acetic acid ( $2\text{ mol l}^{-1}$ )  
dilute hydrochloric acid ( $2.4\text{ mol l}^{-1}$ )  
magnesium chloride  
magnesium hydroxide  
sodium acetate  
sodium hydroxide

*Tray A*  
glass stirring rod  
test-tubes (eight)

*Tray B*  
measuring cylinder,  $25\text{ cm}^3$

*Tray C*  
measuring spoon (spatula-type)  
test-tube brush  
test-tube rack  
wash bottle

*Part 1*

Fill the rounded bottom of one test-tube with magnesium chloride, and add two pellets of sodium hydroxide to another. Add distilled water from the wash bottle to both test-tubes to a depth of about 2 cm, and shake or stir until the solids have dissolved. Now pour the contents of one test-tube into the other. Note what happens in your Notebook.

*Part 2*

Stir the contents of the test-tube from Part 1 for about 30 seconds, and allow the solid to settle. Carefully tilt the tube to pour away as much clear liquid as possible, while leaving the solid in the test-tube. Now pour  $5\text{ cm}^3$  of dilute hydrochloric acid into the measuring cylinder. Add it, approximately  $1\text{ cm}^3$  at a time to the test-tube, shaking or stirring between the successive additions of acid. Note what happens in your Notebook.

(You may also try this experiment with the suspension of magnesium hydroxide in its saturated solution which you retained from Experiment 1. However, because the suspension is not freshly prepared, it may react rather slowly.)

*Part 3*

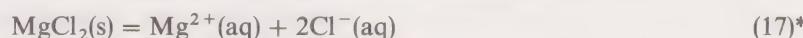
Fill the rounded bottom of a test-tube with sodium acetate, and add distilled water to a depth of about 2 cm. Shake until the solid dissolves. To two other test-tubes, add a 2 cm depth of dilute acetic acid. To one of these two tubes, add two pellets of sodium hydroxide, and shake until the pellets dissolve. Now pour the contents of each test-tube on to a clean, dry saucer. Compare the smell of the acetic acid that has been treated with sodium hydroxide with that of untreated acetic acid and with that of sodium acetate solution.

Your results should raise several questions. For instance, what is the substance produced in Part 1? This is answered in Section 4.3. The changes observed in Parts 2 and 3 can be thought of as a shift in the positions of certain chemical equilibria. What equations describe these equilibria, and why do the shifts occur in the particular directions that they do? These questions are dealt with in Sections 4.4 and 4.5.

### 4.3 TRYING TO BEAT THE EQUILIBRIUM SYSTEM

The amount of magnesium hydroxide that we can dissolve in water is limited by the equilibrium in Equation 21. And as we have seen, this equilibrium lies well over to the left-hand side of the equation: magnesium hydroxide is very sparingly soluble at  $25^\circ\text{C}$ , and only very low concentrations of  $\text{Mg}^{2+}\text{(aq)}$  and  $\text{OH}^-\text{(aq)}$  coexist in the saturated solution. A solution containing higher concentrations of *both* these ions seems to be unobtainable, but we shall make one last attempt to get it.

Unlike  $\text{Mg(OH)}_2$ , both  $\text{MgCl}_2$  and  $\text{NaOH}$  are very soluble in water, and you have already seen that their solutions contain ions:



## PRECIPITATE

## LE CHATELIER'S PRINCIPLE

So by dissolving  $MgCl_2$  in water, you can obtain a solution containing a high concentration of  $Mg^{2+}(aq)$ . Likewise, from  $NaOH$ , you can obtain a solution containing a high concentration of  $OH^-(aq)$ . If you now mix the two, the result will be a solution in which high concentrations of  $Mg^{2+}(aq)$  and  $OH^-(aq)$  exist together. These concentrations will be far higher than those obtainable by dissolving  $Mg(OH)_2(s)$  in water, far higher, in other words, than Equilibrium 21 allows.

- What happened when you tried this experiment?
- A white solid suddenly appears when the two clear solutions are mixed (Experiment 2 Part 1).

When, as a result of a chemical reaction, a solid appears in what was previously a clear solution, the solid is called a **precipitate**. In this case the precipitate is magnesium hydroxide and it shows that you cannot beat the equilibrium system in this way. What happens is that, at these high concentrations,  $Mg^{2+}(aq)$  and  $OH^-(aq)$  combine to form  $Mg(OH)_2(s)$ :



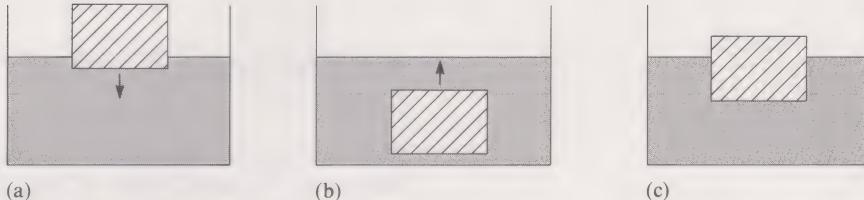
The concentrations therefore drop until they are comparable with those obtained by dissolving  $Mg(OH)_2(s)$  in water. At this point, precipitation of  $Mg(OH)_2$  stops, and the chemical equilibrium described by Equation 21 once more exists. Throughout this drama, the other ions present in your mixed solutions,  $Na^+(aq)$  and  $Cl^-(aq)$ , remain in solution because, unlike  $Mg(OH)_2$ ,  $NaCl$  is freely soluble in water.

There are two general lessons to be learnt from this experiment. First, we can make a saturated solution of magnesium hydroxide either by allowing the  $Mg(OH)_2(s)$  on the left of Equation 21 to dissolve in water, or by making the  $Mg^{2+}(aq)$  and  $OH^-(aq)$  on the right combine to form a precipitate. Thus chemical equilibrium, the state of balance between the two sides of the chemical equation, can be approached from two opposed directions: we can start from either side of the equation. As we saw in Section 4.2, at equilibrium the rates of the two opposed processes are equal and there is no net transfer of material from one side of the equation to the other.

Secondly, you now know that if, by mixing solutions of two readily soluble ionic compounds, you mix the ions derived from a very sparingly soluble compound, that compound will be precipitated.

Finally, notice that the equilibrium position in our hydrostatic analogy can, like chemical equilibrium, be approached from two opposed directions (Figure 4). The wooden block can either be let fall, or submerged and allowed to rise. However, as noted at the end of Section 4.2, the final equilibrium state does *not* have the dynamic quality of chemical equilibrium. There, the analogy breaks down.

**FIGURE 4** Like chemical equilibrium, this hydrostatic equilibrium (c) can be approached from two opposed directions. The wooden block can be let fall (a), or submerged and allowed to rise (b). But the equilibrium state (c) does *not* have the dynamic quality of chemical equilibrium.



#### 4.4 LE CHATELIER'S PRINCIPLE

You now know that Part 1 of Experiment 2 yielded a precipitate of magnesium hydroxide in contact with its aqueous solution. Part 2 of Experiment 2 showed that when hydrochloric acid is added to this precipitate, the solid hydroxide dissolves. There is an especially illuminating way of looking at this change. Before the acid was added, we had the equilibrium

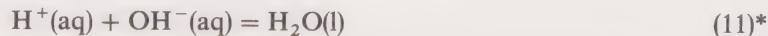


We argue that the addition of acid then *disturbs* this equilibrium, and that the subsequent dissolving of  $\text{Mg(OH)}_2(\text{s})$  is a *response to the disturbance*.

In what way does the addition of acid disturb Equilibrium 21? From Section 2.2 you know that acids are a source of  $\text{H}^+(\text{aq})$ , which can react with one of the ions in Equation 21.

Which one?

$\text{H}^+(\text{aq})$  combines with  $\text{OH}^-(\text{aq})$  in the fundamental Arrhenius acid–base reaction:



This destruction of  $\text{OH}^-(\text{aq})$  lowers the concentration of this ion below the value that was present in the saturated solution of magnesium hydroxide: the equilibrium of Equation 21 is disturbed. How does the system respond to the disturbance? There is a principle that answers this question. It is called **Le Chatelier's principle**, after Henri Le Chatelier (1850–1936), a French mining engineer and chemist who first formulated it in 1888. We state it as follows:

#### LE CHATELIER'S PRINCIPLE

When a system in equilibrium is subjected to an external constraint, the system responds in a way that tends to lessen the effect of the constraint.

Let us use this principle to explain the effect of acid on Equilibrium 21.

- What external constraint does the equilibrium experience when  $\text{H}^+(\text{aq})$  is added?
- As noted above, the concentration of  $\text{OH}^-(\text{aq})$ , one of the ions present in Equilibrium 21, is lowered.

How can the system respond so as to lessen the effect of this constraint? At equilibrium, the right to left, and left to right reactions in Equation 21 proceed at equal rates. The lowering of the concentration of  $\text{OH}^-(\text{aq})$  throws the equilibrium out of balance and destroys this equality, so material must be transferred from one side of the equation to the other. Le Chatelier's principle tells us that this movement occurs from left to right:  $\text{Mg(OH)}_2(\text{s})$  dissolves and produces  $\text{OH}^-(\text{aq})$ . It does so because, by this means, the external constraint—the loss of  $\text{OH}^-(\text{aq})$  caused by addition of acid—is lessened.

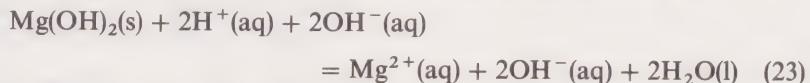
What net change is produced by all this activity? We started with Equilibrium 21 which has  $2\text{OH}^-(\text{aq})$  on the right-hand side. When hydrogen ions were added, we argued that they reacted with this ' $2\text{OH}^-(\text{aq})$ ' so we shall write the change by doubling Equation 11:



As we have seen, Le Chatelier's principle tells us that this disturbance is followed by the net dissolution of more  $\text{Mg(OH)}_2(\text{s})$ :



So the total change is the sum of Equations 22 and 20. Adding the two left-hand sides and two right-hand sides together separately, we get



- Reduce this equation to a simpler form.

STRONG ELECTROLYTE

STRONG ACID

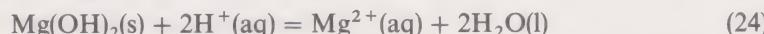
STRONG BASE

WEAK ELECTROLYTE

WEAK ACID

ACID STRENGTH

Following our treatment of Equation 10, we eliminate the  $2\text{OH}^-(\text{aq})$  on each side:

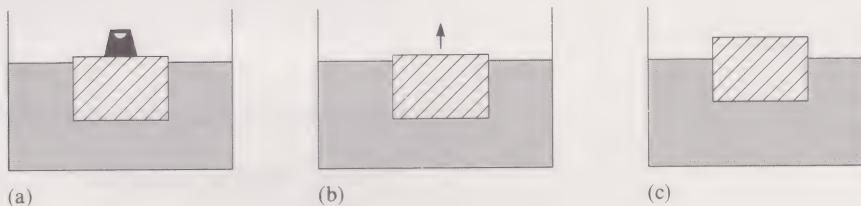


This equation is the best description of the overall change that occurs when acid is added to a suspension of  $\text{Mg(OH)}_2(\text{s})$  in water. As we have seen, it can be derived via an application of Le Chatelier's principle.

**ITQ 6** Suppose that solid  $\text{MgCl}_2$  is dissolved in a saturated solution of magnesium hydroxide, like the one you retained from Experiment 1. Measurements then show that the hydroxide ion concentration in the saturated solution is lowered. Explain this by applying Le Chatelier's principle.

Analyses of these applications of Le Chatelier's principle can be found in our hydrostatic equilibrium. Suppose that this time, the wooden block supports a small metal object (Figure 5a). At equilibrium the weight of metal and wood is exactly balanced by an upthrust or upward force from the water. Removal of the object (Figure 5b) is an external constraint. It disturbs the equilibrium by making the weight less than the upthrust. But the system now reacts to lessen the effect of the constraint: the block rises, and as it does so, the upthrust is lessened. Eventually weight and upthrust are once more in balance at a new equilibrium position (Figure 5c).

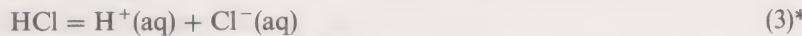
FIGURE 5 A system in hydrostatic equilibrium (a) is subjected to an external constraint by removal of the metal object (b). The block moves upwards to a new equilibrium position (c).



## 4.5 EQUILIBRIUM IN A SOLUTION OF A WEAK ACID

The two examples of chemical equilibrium that we discussed in Sections 4 to 4.4 were set up by adding electrolytes to water: both solid  $\text{NaCl}$  and  $\text{Mg(OH)}_2$  dissolve and form aqueous ions. Sodium chloride and magnesium hydroxide, however, are electrolytes of a special kind, in that virtually *all* of the substance that dissolves breaks down into ions. Such substances are called **strong electrolytes**.

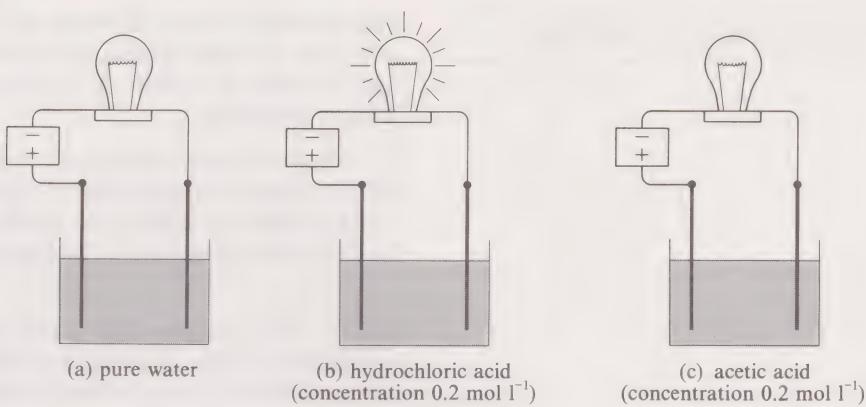
Most of the electrolytes that you have met so far have been of the strong variety. This is true, for example, of all salts, substances that, as we saw in Section 2.3, result from the combination of the cation of a base with the anion of an acid. Some acids, such as  $\text{HCl}$  and  $\text{HNO}_3$ , are also strong electrolytes: all the dissolved  $\text{HCl}$  and  $\text{HNO}_3$  is broken up into ions, one variety of which is  $\text{H}^+(\text{aq})$ :



Substances like  $\text{HCl}$  and  $\text{HNO}_3$ , which are both strong electrolytes and acids, are called **strong acids**. Likewise, substances like  $\text{Mg(OH)}_2$  and  $\text{NaOH}$  are strong electrolytes by virtue of a dissociation which yields  $\text{OH}^-(\text{aq})$ . They are called **strong bases**.

But not all acids and bases are strong electrolytes. To illustrate this, let us consider an experiment that you could do with the strong acid,  $\text{HCl}$ .

Earlier in this Unit (Figure 1), we noted that when some hydrochloric acid of concentration about  $2.0\text{ mol l}^{-1}$  is added to water, the conductivity of the water is greatly increased.



**FIGURE 6** (a) Pure water is tested as in Experiment 4 of Units 13–14; (b) dilute hydrochloric acid is added until the acid concentration is about  $0.2\text{ mol l}^{-1}$ : the bulb lights up; (c) the exercise is repeated with dilute acetic acid: the bulb remains unlit.

- How was this increased conductivity detected?
  - The bulb in the electric circuit shown in Figure 6b lit up.

The greatly increased conductivity and the illumination of the bulb are made possible by the high concentration of ions in the HCl solution. This high concentration is due, in turn, to the fact that HCl is a strong acid: in solution it dissociates completely into ions. Now your Experiment Kit also contains acetic acid of concentration  $2\text{ mol l}^{-1}$ . If you repeat the hydrochloric acid experiment with this acetic acid, you will find that this time the bulb does *not* light up (Figure 6c).

- Does acetic acid solution contain any ions?
  - In Experiment 1, it turned blue litmus red: it must contain some  $\text{H}^+(\text{aq})$ .
  - Why then did the bulb not light up?
  - Unlike dissolved HCl, the dissolved acetic acid is *not* completely broken up into ions so the conductivity of water is not increased enough to illuminate the bulb.

Acetic acid has a complex formula  $C_2H_4O_2$ , which you will study further in Units 17–18. If it splits up in water into ions, one of the hydrogens breaks off as  $H^+(aq)$ , and the rest of the formula is left as the acetate anion,  $C_2H_3O_2^-(aq)$ . In this Unit, we shall keep things simple by using the symbol Ac for the collection of atoms  $C_2H_3O_2$  (note that Ac is *not* a chemical element). Acetic acid is then denoted by HAc, thus emphasizing the single hydrogen that can be ionized in water, and the acetate ion becomes  $Ac^-(aq)$ .

Now although acetic acid dissolves readily in water, the experiments in Figure 6 suggest that only a little of the dissolved acid breaks up into the ions  $H^+(aq)$  and  $Ac^-(aq)$ . What we have in the solution is an equilibrium between the aqueous undissociated acid, and its aqueous ions:



Furthermore, the equilibrium inclines towards the left-hand side of this equation: most dissolved acid is in the form of neutral undissociated molecules, HAc(aq). Substances that are only *partly* broken down into ions when they dissolve in water are called **weak electrolytes**. If, like acetic acid, they are also acids, we call them **weak acids** to distinguish them from the strong acids, which are completely dissociated. (Weak bases also exist, but they are not discussed explicitly in this Course.)

Finally, in this context, note the important distinction between **strength** and **concentration**. A solution is concentrated if the concentration of the solute in the solution is high. An electrolyte is strong if, when dissolved, it is completely dissociated into ions. We can therefore have concentrated solutions of weak electrolytes: an acetic acid solution of concentration  $10\text{ mol l}^{-1}$  is an example. Conversely, we can have dilute solutions of strong electrolytes: a saturated solution of magnesium hydroxide is dilute because the solid is

## EQUILIBRIUM CONSTANT

only sparingly soluble in water, but what dissolves is completely dissociated into ions. So when talking about the concentration of a solution, it's a good idea to refer to 'dilute' or 'concentrated' solutions, rather than 'weak' or 'strong' solutions.

In Section 4.4, we explained the results of Part 2 of Experiment 2 by applying Le Chatelier's principle to the equilibrium of Equation 21. In ITQ 7, you are asked to explain the results of Part 3 of Experiment 2 by applying Le Chatelier's principle to the equilibrium of Equation 25.

**ITQ 7** The characteristic smell of acetic acid is due to the presence of undissociated HAc molecules in the solution. Use Le Chatelier's principle to explain the following observations:

- When sodium hydroxide is dissolved in acetic acid, the acid's vinegar-like smell is much diminished;
- When solid sodium acetate, NaAc, is dissolved in acetic acid solution, measurements show that the hydrogen ion concentration of the solution is greatly decreased.

## SUMMARY OF SECTION 4

- A system in chemical equilibrium appears to be quiescent at constant temperature.
- Chemical equilibrium is dynamic: the appearance of quiescence is the result of two opposed chemical processes occurring at equal rates.
- A state of chemical equilibrium can be approached from two opposed directions, corresponding to the two opposed processes.
- When a system in chemical equilibrium is subjected to an external constraint, the system responds in a way that tends to lessen the effect of the constraint (Le Chatelier's principle).
- All these points can be demonstrated by two important kinds of equilibrium system: the saturated solution of a strong electrolyte, and the equilibrium between the solution of a weak acid and its aqueous ions.

**SAQ 6** Table 2 divides some lead (Pb), barium (Ba) and alkali metal (Na and K) salts into two categories: those that are readily soluble in water and those that are very sparingly soluble in water. The colours of the very sparingly soluble compounds are given in brackets.

TABLE 2 List of readily soluble and very sparingly soluble salts for SAQ 6. Colours of the very sparingly soluble salts are given in brackets. All of the freely soluble salts consist of colourless crystals

Freely soluble	Very sparingly soluble
BaCl <sub>2</sub> , Ba(NO <sub>3</sub> ) <sub>2</sub> ,	BaSO <sub>4</sub> (white)
Na <sub>2</sub> CO <sub>3</sub> , NaCl,	BaCO <sub>3</sub> (white)
NaNO <sub>3</sub> , Na <sub>2</sub> SO <sub>4</sub> ,	PbCl <sub>2</sub> (white)
KI, KNO <sub>3</sub> ,	PbI <sub>2</sub> (yellow)
Pb(NO <sub>3</sub> ) <sub>2</sub>	PbCO <sub>3</sub> (white)
	PbSO <sub>4</sub> (white)

State whether any visible chemical reaction occurs when aqueous solutions of the following compounds are mixed. If a reaction occurs, write an equation for it:

- Barium chloride, BaCl<sub>2</sub>, and sodium sulphate, Na<sub>2</sub>SO<sub>4</sub>
- Barium nitrate, Ba(NO<sub>3</sub>)<sub>2</sub>, and sodium chloride, NaCl
- Lead nitrate, Pb(NO<sub>3</sub>)<sub>2</sub>, and potassium iodide, KI
- Lead nitrate, Pb(NO<sub>3</sub>)<sub>2</sub>, and sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>

**SAQ 7** Hydrogen chloride gas, HCl, is dissolved in an aqueous solution of acetic acid. Will the concentrations of the acetate ion,  $\text{Ac}^-(\text{aq})$ , and the undissociated acid,  $\text{HAc}(\text{aq})$ , rise or fall? (Hint: HCl is a strong electrolyte.)

**SAQ 8** Write a balanced equation for the reaction between hydrogen gas,  $\text{H}_2$ , and nitrogen gas,  $\text{N}_2$ , to form gaseous ammonia,  $\text{NH}_3$ .

$\text{NH}_3$  is very soluble in water, but  $\text{H}_2$  and  $\text{N}_2$  are only slightly so. Suppose you have an equilibrium mixture of  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{NH}_3$ , and the mixture is then washed with a spray of water. Use Le Chatelier's principle to predict what will happen.

**SAQ 9** Assign the aqueous solutions (i)–(v) to the following categories: (a) a dilute solution of a weak electrolyte; (b) a concentrated solution of a weak or non-electrolyte; (c) a dilute solution of a strong electrolyte; (d) a concentrated solution of a strong electrolyte.

- (i) Hydrochloric acid of concentration  $12 \text{ mol l}^{-1}$
- (ii) Acetic acid of concentration  $0.002 \text{ mol l}^{-1}$
- (iii) A saturated solution of magnesium hydroxide
- (iv) A saturated solution of sugar
- (v) A saturated solution of potassium iodide

## 5 THE EQUILIBRIUM CONSTANT

Let us look again at the experimental observations in ITQ 7. We began with a solution of acetic acid in which there exists the equilibrium



We then increased the concentration of  $\text{Ac}^-(\text{aq})$  by dissolving solid sodium acetate in the solution. This threw the system out of balance, and material was transferred from one side of Equation 25 to the other.

- How did this transfer affect the concentrations of  $\text{HAc}(\text{aq})$  and  $\text{H}^+(\text{aq})$ ?
- The system responded by trying to mitigate the increase in the concentration of  $\text{Ac}^-(\text{aq})$ . Some  $\text{H}^+(\text{aq})$  therefore destroyed some  $\text{Ac}^-(\text{aq})$  by combining with it to form  $\text{HAc}(\text{aq})$ . Thus the concentration of  $\text{H}^+(\text{aq})$  was lowered, and that of  $\text{HAc}(\text{aq})$  was increased. Then a new position of equilibrium was reached, and the changes stopped.

Notice that this explanation is not quantitative: it simply talks of increases and decreases. Can it therefore be expressed in a more quantitative way? The answer is that it can, because whenever  $\text{HAc}(\text{aq})$  is in equilibrium with  $\text{H}^+(\text{aq})$  and  $\text{Ac}^-(\text{aq})$ , there is a precise, numerical relationship between the concentrations of the three species. We shall begin by simply telling you what this relationship is.

Suppose we write the concentration of a species in the solution by enclosing the symbol for the species in square brackets. Thus the concentration of  $\text{HAc}(\text{aq})$  is written  $[\text{HAc}(\text{aq})]$ . Suppose also that we have a solution in which  $\text{HAc}(\text{aq})$  is in equilibrium with  $\text{H}^+(\text{aq})$  and  $\text{Ac}^-(\text{aq})$ :



It turns out that there is a constant,  $K$ , given by

$$K = \frac{[\text{H}^+(\text{aq})][\text{Ac}^-(\text{aq})]}{[\text{HAc}(\text{aq})]} \quad (26)$$

At  $25^\circ\text{C}$ ,  $K = 1.8 \times 10^{-5} \text{ mol l}^{-1}$ . This constant is called the **equilibrium constant** of the system in Equation 25. In this case, it is created by multiplying the concentrations of the two species on the right of the equation together, and dividing them by the concentration of the species on the left.

## ACID DISSOCIATION CONSTANT

How can this help us to understand the response of the equilibrium to the increase in  $[Ac^-(aq)]$ ? Because  $[Ac^-(aq)]$  appears in the numerator of the expression on the right of Equation 26, the immediate result of the increase is to raise the value of this expression above the equilibrium value of  $1.8 \times 10^{-5} \text{ mol l}^{-1}$ . This means that the system is no longer at equilibrium: to return to equilibrium, the value of the expression must be lowered back to  $1.8 \times 10^{-5} \text{ mol l}^{-1}$ .

- How can the transfer of material from the right to the left of Equation 25 achieve this?
- If some  $H^+(aq)$  and  $Ac^-(aq)$  combine to form  $HAc(aq)$ , the two concentrations in the numerator will decrease, and the single concentration in the denominator will increase. *All three changes lower the numerical value of the expression.* This process continues until the value is once more  $1.8 \times 10^{-5} \text{ mol l}^{-1}$ .

In ITQ 7, we used Le Chatelier's principle to explain changes that occur when the concentration of a species in Equilibrium 25 is altered. You should now be able to see that these changes are a consequence of the requirement that Equation 26 must hold at equilibrium.

Finally, notice that in the particular case of Equation 26, the equilibrium constant has units of  $\text{mol l}^{-1}$ .

- Can you see from Equation 26 why this is so?
- Each individual concentration in Equation 26 is expressed in  $\text{mol l}^{-1}$ . As two concentrations are multiplied together on top, and then divided by a single concentration at the bottom, the units of  $K$  will be  $\text{mol l}^{-1}$ .

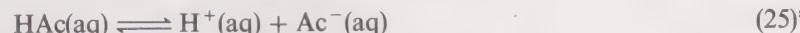
**ITQ 8** You observed the effect of dissolved sodium hydroxide on Equilibrium 25 in Part 3 of Experiment 2: the smell of undissociated acetic acid molecules was diminished. Use Equation 26 to explain this result.

## 5.1 THE SIZE OF THE EQUILIBRIUM CONSTANT

You now know that when pure acetic acid is added to water, it forms undisassociated molecules,  $HAc(aq)$ , some of which then break up into ions:



This overall change continues until the equilibrium



is reached. Then at  $25^\circ\text{C}$ ,

$$\frac{[H^+(aq)][Ac^-(aq)]}{[HAc(aq)]} = 1.8 \times 10^{-5} \text{ mol l}^{-1} \quad (28)$$

Suppose that the amount of acetic acid that we add is just enough to make the final equilibrium concentration of *undissociated* acid,  $[HAc(aq)]$ , equal to  $1 \text{ mol l}^{-1}$ . Let us work out what the equilibrium concentrations of  $H^+(aq)$  and  $Ac^-(aq)$  would be in this case.

- First, what can you say about the *relative* values of  $H^+(aq)$  and  $Ac^-(aq)$ ?
- Every  $HAc$  molecule that dissociates puts one  $H^+(aq)$  and one  $Ac^-(aq)$  into the solution. The numbers of the two kinds of ion, and therefore their concentrations, must be equal. Thus  $[H^+(aq)] = [Ac^-(aq)]$ .

We shall use the symbol  $y$  for this common concentration of  $H^+(aq)$  and  $Ac^-(aq)$ . As  $[HAc(aq)] = 1 \text{ mol l}^{-1}$ , Equation 28 tells us that,

$$\frac{y \times y}{1 \text{ mol l}^{-1}} = 1.8 \times 10^{-5} \text{ mol l}^{-1}$$

$$y^2 = 1.8 \times 10^{-5} \text{ mol}^2 \text{l}^{-2}$$

$$y = 4.2 \times 10^{-3} \text{ mol l}^{-1}$$

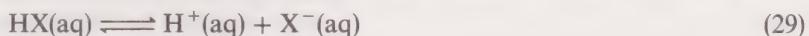
Thus, every litre of the equilibrium solution contains 1 mole of HAc(aq), 0.0042 mole of H<sup>+</sup>(aq) and 0.0042 mole of Ac<sup>-</sup>(aq).

- When the solution was first made up by adding acetic acid to water, how many moles of acetic acid were needed to make each litre of solution?
- 1.0042 moles. 1 mole is needed to form the undissociated HAc(aq). Every molecule of HAc that dissociates forms one H<sup>+</sup>(aq) and one Ac<sup>-</sup>(aq). Therefore the residual 0.0042 mole is sufficient to form the 0.0042 mole of H<sup>+</sup>(aq), and the 0.0042 mole of Ac<sup>-</sup>(aq) in each litre.

The experiment pictured in Figure 6 suggested that very little of the dissolved acetic acid is dissociated into ions. We now have a quantitative reinforcement of this point. In the solution that we have just discussed, only about 0.4% of the dissolved acetic acid breaks up into ions. Reaction 27 does not proceed very far before the equilibrium of Equation 25 is reached: the equilibrium position lies well over to the left of Equation 25.

In the context of the calculation, we obtained a small percentage dissociation because  $K$ , the expression on the left of Equation 28, is very small. Study the calculation again to make sure you understand this; SAQ 10 at the end of this section provides further confirmation. Thus the size of  $K$  is an indication of how far Reaction 27 goes, that is, of the *strength* of this particular weak acid.

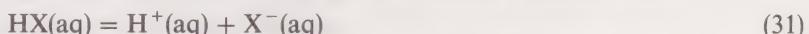
Now there are many other acids that, like acetic acid, break up in water into H<sup>+</sup>(aq) and a singly charged anion, which we can write X<sup>-</sup>(aq). As with acetic acid, in their aqueous solutions there exists the equilibrium



for which we can write an equilibrium constant  $K_a$ ,

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{X}^-(\text{aq})]}{[\text{HX(aq)}]} \quad (30)$$

where  $K_a$  is an indication of how far the following reaction goes:



This time we have added a subscript 'a' to  $K$  in recognition of the fact that we are dealing with the equilibrium constant of a particular kind of reaction—the dissociation of an acid. Not surprisingly then,  $K_a$  is called the **acid dissociation constant**.

Some values of  $K_a$  for acids of the type HX are shown in Table 3. Note first that hydrochloric and nitric acids are simply labelled 'strong acid'.

TABLE 3 Values of  $K_a$  for selected acids at 25 °C

Acid	Dissociation equilibrium	$K_a/\text{mol l}^{-1}$
hydrochloric	HCl(aq) = H <sup>+</sup> (aq) + Cl <sup>-</sup> (aq)	strong acid
nitric	HNO <sub>3</sub> (aq) = H <sup>+</sup> (aq) + NO <sub>3</sub> <sup>-</sup> (aq)	strong acid
iodic	HIO <sub>3</sub> (aq) ⇌ H <sup>+</sup> (aq) + IO <sub>3</sub> <sup>-</sup> (aq)	$1.7 \times 10^{-1}$
nitrous	HNO <sub>2</sub> (aq) ⇌ H <sup>+</sup> (aq) + NO <sub>2</sub> <sup>-</sup> (aq)	$4.5 \times 10^{-4}$
acetic	HAc(aq) ⇌ H <sup>+</sup> (aq) + Ac <sup>-</sup> (aq)	$1.8 \times 10^{-5}$
hypochlorous	HClO(aq) ⇌ H <sup>+</sup> (aq) + ClO <sup>-</sup> (aq)	$2.9 \times 10^{-8}$

- Look back at Equation 30. Can you suggest why values of  $K_a$  are not quoted in these cases?
- These acids are completely dissociated in aqueous solution: there is no evidence for any HX(aq). If [HX(aq)] is zero,  $K_a$  is infinite, so acid dissociation constants are not used with these strong electrolytes.

It is therefore meaningless to assign relative strengths to strong acids in aqueous solution: hydrochloric acid and nitric acid are equally strong. But the other  $K_a$  values in Table 3 are finite: these acids are weak acids, which are not completely dissociated into ions in aqueous solution, and their relative strengths can be compared in terms of the values of  $K_a$ . Thus iodic acid is stronger than nitrous acid, which is stronger than acetic acid.

## SUMMARY OF SECTION 5

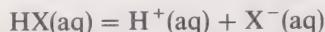
- 1 In an aqueous solution of an acid, HX, *at equilibrium*, the quantity

$$\frac{[\text{H}^+(\text{aq})][\text{X}^-(\text{aq})]}{[\text{HX}(\text{aq})]}$$

always has a constant value,  $K_a$ , which is known as the acid dissociation constant or, most generally, as the equilibrium constant.

- 2 The way in which the weak acid system responds to changes in the concentration of HX(aq),  $\text{H}^+(\text{aq})$ , and  $\text{X}^-(\text{aq})$  can be regarded as an attempt to maintain the quantity in question at the equilibrium value,  $K_a$ .

- 3  $K_a$  is a measure of how far the following reaction proceeds before equilibrium is attained:



**SAQ 10** Iodic acid,  $\text{HIO}_3$ , is dissolved in water until the concentration of undissociated acid,  $[\text{HIO}_3(\text{aq})]$ , is  $1 \text{ mol l}^{-1}$ . Use the  $K_a$  value in Table 3 to calculate (i) values for  $[\text{H}^+(\text{aq})]$  and  $[\text{IO}_3^-(\text{aq})]$ , and (ii) the percentage of the total dissolved acid that is broken down into ions at  $25^\circ\text{C}$ . (Hint: use your answer to (i) to work out the sum of the amounts of dissociated and undissociated acid in one litre of the solution.)

**SAQ 11** 0.1 mole of an acid HX is dissolved in water and the solution is made up to one litre. In this solution, half of the dissolved acid is in an undissociated state. What are the concentrations of HX(aq),  $\text{H}^+(\text{aq})$  and  $\text{X}^-(\text{aq})$  in the solution? What is the value of  $K_a$  for the acid?

Compare your answer with the value of  $K_a$  for nitrous acid ( $\text{HNO}_2$ ) in Table 3. What do you conclude about the proportion of undissociated acid in an aqueous solution of  $\text{HNO}_2$  of concentration  $0.1 \text{ mol l}^{-1}$ ?

**SAQ 12** Consider the solution of  $\text{HNO}_2$  of concentration  $0.1 \text{ mol l}^{-1}$  referred to in SAQ 11. Suppose it is compared with a solution of nitric acid,  $\text{HNO}_3$ , of concentration  $0.05 \text{ mol l}^{-1}$ ; which of the following statements is correct?

- The  $\text{HNO}_2(\text{aq})$  solution is the more concentrated.
- $\text{HNO}_2(\text{aq})$  is the stronger acid.
- $[\text{H}^+(\text{aq})]$  is higher in the  $\text{HNO}_2(\text{aq})$  solution.

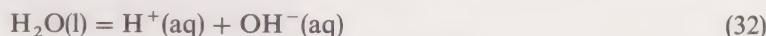
## 6 WHAT ABOUT THE SOLVENT?

When, in Section 5.1, we used  $K_a$  to calculate the hydrogen ion concentration, we assumed that all the  $\text{H}^+(\text{aq})$  originated from dissolved acid: water, the solvent, was regarded as a background medium which, by itself, supplies no hydrogen ions. This assumption is not correct, but in Section 5.1 that did not matter, because the amount of hydrogen ions provided by the water was negligible in comparison with the amount supplied by the acid. In solutions of much lower acidity this is not the case, and variations in hydrogen ion concentration cannot be understood without considering the contribution of the solvent. Solutions of this kind fall as rain, occur in rivers and seas, and circulate through plants and animals. Very small changes in their

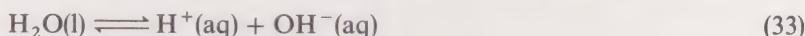
hydrogen ion concentration can have a profound and sometimes lethal effect on living things. Clearly then, we must try to understand how the solvent can influence hydrogen ion concentrations.

The assumption that, in problems of acidity, water can be regarded as mere background implies that pure water contains no  $\text{H}^+(\text{aq})$ . This is consistent with Experiment 4 of Units 13–14: when water was tested with the circuit shown in Figure 6, the bulb did not light up. However, as Figure 6 shows, acetic acid solution does not light the bulb either, and we now know that it contains significant concentrations of ions. Perhaps therefore, any ion concentrations in pure water are too small to be detected by this relatively insensitive test. This idea is supported by common knowledge: water in contact with exposed electric wiring is dangerous because it can transmit electric shocks. Such conductivity supports the idea that water contains *some* ions.

- What ions might be present in pure water?
- $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  are now very familiar to you. An obvious equation for the breakdown of a water molecule into ions is



The picture of pure water that all this conjures up is of a medium that is mainly water molecules,  $\text{H}_2\text{O(l)}$ , with small amounts of  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  also present. In other words, in water there is an equilibrium:



The detectable, but very small conductivity of water suggests that only tiny amounts of  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  are present. The left to right reaction of Equation 32 does not go very far so the equilibrium position in Equation 33 lies well over to the left. Since, from Section 4.3, we know that equilibrium can be approached from two opposed directions, this must mean that the reverse, right to left reaction must go a long way.

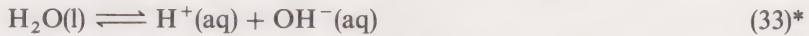
- What evidence do you have that this is so?
- We have, until now, regarded the fundamental Arrhenius acid–base reaction



as essentially complete, and this assumption has held good throughout the discussion so far.

## 6.1 THE ION PRODUCT OF WATER

Various pieces of evidence therefore support a picture of water as an equilibrium system,



in which equilibrium lies far to the left. This equilibrium corresponds closely to that for a weak acid,  $\text{HX}$ , in Section 5.1: the undissociated acid occurs on the left, and  $\text{H}^+(\text{aq})$  and  $\text{X}^-(\text{aq})$  on the right.

- Write down an expression for the equilibrium constant for Equation 33.
- Following Equation 30,

$$K = \frac{[\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O(l)}]} \quad (34)$$

The terms  $[\text{H}^+(\text{aq})]$  and  $[\text{OH}^-(\text{aq})]$  represent the molar ion concentrations in water, but what does  $[\text{H}_2\text{O(l)}]$  mean? Well, according to the measure of concentration that we have adopted,  $[\text{H}_2\text{O(l)}]$  is the number of moles of water in one litre of water. One litre of water has a mass of 1 000 g, and the molar mass of water is 18 g. So, ignoring the minute amount of water

## ION PRODUCT OF WATER

## NEUTRAL SOLUTION

## LOGARITHM TO THE BASE 10

present as ions,

$$\begin{aligned} [\text{H}_2\text{O(l)}] &= \frac{1\,000}{18.0} \text{ mol l}^{-1} \\ &= 55.6 \text{ mol l}^{-1} \end{aligned}$$

In Equation 34 this constant term is *by convention* taken over to the left-hand side, so that Equation 34 becomes

$$K[\text{H}_2\text{O(l)}] = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$$

The combination  $K[\text{H}_2\text{O(l)}]$  is called the **ion product of water** and is written  $K_w$ . The experimentally determined value of  $K_w$  is  $1.0 \times 10^{-14} \text{ mol}^2 \text{l}^{-2}$  at  $25^\circ\text{C}$ . Thus

$$K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1.0 \times 10^{-14} \text{ mol}^2 \text{l}^{-2} \quad (35)$$

Notice, first of all, that the size of this constant does indeed limit the concentrations of hydrogen and hydroxide ions that can coexist in pure water. In water, the  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  ions are supplied by the dissociation of water: every molecule that dissociates forms one hydrogen and one hydroxide ion, so if  $[\text{H}^+(\text{aq})]$  is  $x$ ,  $[\text{OH}^-(\text{aq})]$  must be  $x$  as well. From Equation 35,

$$K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = x^2 = 1.0 \times 10^{-14} \text{ mol}^2 \text{l}^{-2}$$

so

$$x = 1.0 \times 10^{-7} \text{ mol l}^{-1}$$

This result shows that in pure water at  $25^\circ\text{C}$ , the hydrogen and hydroxide ion concentrations are both  $1.0 \times 10^{-7} \text{ mol l}^{-1}$ —very small values indeed! Roughly speaking, they mean that only one in every thousand million water molecules is ionized—Reaction 32 proceeds to only a tiny extent.

However, the implications of Equation 35 are rather more wide ranging than this. You have seen that an acid solution is one in which  $[\text{H}^+(\text{aq})]$  is high, whereas a basic solution is one in which  $[\text{OH}^-(\text{aq})]$  is high. Equation 35 expresses this idea in a quantitative way: it imposes a limitation on the concentrations of hydrogen and hydroxide ions that can coexist in *any* aqueous solution, not simply in pure water.

Consider, for example, an aqueous solution of hydrochloric acid of concentration  $0.1 \text{ mol l}^{-1}$ . From Section 5.1, we know that HCl is a strong acid, which is completely dissociated into ions. Thus, the concentration of  $\text{H}^+(\text{aq})$  ions in the solution is  $0.1 \text{ mol l}^{-1}$ .

- What is the concentration of  $\text{OH}^-(\text{aq})$  ions in this solution?
- It is  $1.0 \times 10^{-13} \text{ mol l}^{-1}$ . This result is arrived at as follows:

$$[\text{H}^+(\text{aq})] = 0.1 \text{ mol l}^{-1} = 1.0 \times 10^{-1} \text{ mol l}^{-1}$$

From Equation 35,

$$K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1.0 \times 10^{-14} \text{ mol}^2 \text{l}^{-2} \quad (35)^*$$

$$\begin{aligned} [\text{OH}^-(\text{aq})] &= \frac{1.0 \times 10^{-14} \text{ mol}^2 \text{l}^{-2}}{1.0 \times 10^{-1} \text{ mol l}^{-1}} \\ &= 1.0 \times 10^{-13} \text{ mol l}^{-1} \end{aligned}$$

- What is the concentration of  $\text{H}^+(\text{aq})$  ions in an aqueous solution of NaOH of concentration  $0.1 \text{ mol l}^{-1}$ ?
- Again, it is  $1.0 \times 10^{-13} \text{ mol l}^{-1}$ . NaOH may also be regarded as completely dissociated in water, so  $[\text{OH}^-(\text{aq})]$  is  $0.1 \text{ mol l}^{-1}$ . From Equation 35,  $[\text{H}^+(\text{aq})]$  must be  $1.0 \times 10^{-13} \text{ mol l}^{-1}$ .

Notice that the hydrogen ion concentration in one aqueous solution may be as much as  $10^{12}$  times greater than that in another, but it always has a finite value, even in strongly basic solutions. Similarly, the hydroxide ion concentration always has a finite value, even in strongly acidic solutions.

How would you define a neutral solution?

■ A **neutral solution** shows neither acidic nor basic properties. This suggests  $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$  as a definition. The value of  $K_w$  suggests further that at  $25^\circ\text{C}$ ,  $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})] = 1.0 \times 10^{-7} \text{ mol l}^{-1}$ . Thus at  $25^\circ\text{C}$  an acidic solution can be defined as one in which  $[\text{H}^+(\text{aq})]$  is greater than  $10^{-7} \text{ mol l}^{-1}$ , and a basic solution is one in which it is less.

**ITQ 9** A little solid calcium hydroxide is dissolved in a litre of water. Assuming that the temperature remains at  $25^\circ\text{C}$  throughout, which three of the statements (a)–(e) are correct?

- (a)  $[\text{OH}^-(\text{aq})]$  increases.
- (b)  $[\text{H}^+(\text{aq})]$  increases.
- (c)  $K_w$  increases.
- (d) The number of undissociated water molecules increases.
- (e)  $[\text{H}^+(\text{aq})]$  decreases.

## 6.2 THE pH SCALE

Try the following thought experiment. Suppose you have one litre of hydrochloric acid solution of concentration  $0.1 \text{ mol l}^{-1}$ : the concentrations of  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  will be those calculated in Section 6.1,  $[\text{H}^+(\text{aq})] = 0.1 \text{ mol l}^{-1}$  and  $[\text{OH}^-(\text{aq})] = 1.0 \times 10^{-13} \text{ mol l}^{-1}$ . Suppose that you now slowly add 0.1 mol of solid sodium hydroxide. A neutralization reaction occurs:  $\text{H}^+(\text{aq})$  is consumed and the acidity of the solution drops. When all of the solid has been added, you end up with a solution of sodium chloride in water. Now the concentrations of  $\text{H}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  will be those for pure water; that is,  $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})] = 1.0 \times 10^{-7} \text{ mol l}^{-1}$ . Thus, on adding the NaOH to the HCl solution, the concentration of  $\text{H}^+(\text{aq})$  decreases by a factor of  $10^6$  (a million) from  $10^{-1}$  to  $10^{-7}$ ; at the same time, the hydroxide ion concentration rises by the same factor. What enormous concentration changes are associated with this simple experiment!

Suppose that you wanted to show graphically how the acidity, that is the concentration of  $\text{H}^+(\text{aq})$ , changes during the course of this experiment: how do you even choose a scale for such a graph, when the quantity of interest changes by six orders of magnitude? Fortunately, there is a way out. As the concentration of  $\text{H}^+(\text{aq})$  drops a million-fold from  $10^{-1}$  to  $10^{-7}$ , this notation shows that the *index* simply drops from  $-1$  to  $-7$ . It looks as if this index might provide a much more manageable measure of concentration and concentration changes when they cover many orders of magnitude. This index of ten is called the **logarithm to the base ten** or the common logarithm of the number in question: it is written as  $\log_{10}$ , or simply as log.

If you have met logarithms before, try the following ITQ to check your understanding, then skip the box that follows. If not, or if you get any of the answers wrong, read on.

**ITQ 10** (a) Write down, without using tables or a calculator, the logarithms to the base ten of the following numbers: 10, 100, 0.001.

(b) Your calculator should have a special key for calculating logarithms to the base ten. Use it to calculate the logarithms of the following numbers: 4, 40, 0.4.

(c) In human blood,  $[\text{H}^+(\text{aq})] = 4.0 \times 10^{-8} \text{ mol l}^{-1}$ . Calculate

$$\log \left\{ \frac{[\text{H}^+(\text{aq})]}{\text{mol l}^{-1}} \right\},$$

that is,  $\log (4.0 \times 10^{-8})$ .

## pH SCALE

## WORKING WITH LOGARITHMS

You have seen, in MAFS 1, that 10 can be written in scientific notation as  $10^1$ . Then according to the definition of a logarithm,

$$\log 10 = \log 10^1 = 1$$

$$\text{Similarly, } \log 100 = \log 10^2 = 2$$

$$\text{and } \log 1\,000 = \log 10^3 = 3$$

You could, of course, continue with this process, but these three examples are sufficient to illustrate an extremely important property of logarithms.

Suppose you start by writing 1 000 as  $(10 \times 100)$  instead of  $(10 \times 10 \times 10)$ . Then

$$\log 1\,000 = \log (10 \times 100) = \log (10^1 \times 10^2)$$

$$\text{but } \log 1\,000 = 3$$

$$\text{So } \log (10^1 \times 10^2) = 3 \quad (36)$$

$$\text{However, } \log 10^1 = 1 \text{ and } \log 10^2 = 2$$

$$\text{So } \log 10^1 + \log 10^2 = 3 \quad (37)$$

Comparing Equations 36 and 37, you can see that

$$\log (10^1 \times 10^2) = \log 10^1 + \log 10^2$$

This is, in fact, a completely general result: *the logarithm of two numbers multiplied together is equal to the sum of the logarithms of each number*, that is

$$\log (x \times y) = \log x + \log y \quad (38)$$

Now, according to the definition of log,

$$\log 0.1 = \log 10^{-1} = -1$$

and

$$\log 0.01 = \log 10^{-2} = -2, \text{ etc.}$$

But what is the logarithm to the base 10 of unity? Well, according to Equation 38, you can write

$$\begin{aligned} \log 1 &= \log (0.1 \times 10) \\ &= \log 10^{-1} + \log 10^1 \\ &= -1 + 1 \\ &= 0 \end{aligned}$$

In other words, 1 can be written in index notion as  $10^0$ .

So, for any number (including unity) that can be expressed as a positive or negative whole number power of ten, the common logarithm can be written down by inspection. This is a skill you must master: for example, you may be required to use it during the examination when calculators are prohibited. The skill is tested in ITQ 11.

You should now know nearly as much about logarithms as you will need for the moment. There remains just one further problem: how do you obtain the logarithm of a number that cannot be expressed as a simple whole number power of ten? Suppose, for example, that you have a solution containing  $[\text{H}^+(\text{aq})] = 4.0 \text{ mol l}^{-1}$ ; what is the value of

$$\log \left\{ \frac{[\text{H}^+(\text{aq})]}{\text{mol l}^{-1}} \right\}$$

in this case? What you need to do is express 4.0 in the form  $10^x$ , but how do you determine the value of  $x$ ? This time you will need your calculator to do it for you. Check that you know how to use it by going back and working through the examples in ITQ 10.

Table 4 shows values of

$$\log \left\{ \frac{[\text{H}^+(\text{aq})]}{\text{mol l}^{-1}} \right\}$$

for hydrogen ion concentrations within the range of interest of most chemists: do not worry about the column labelled pH for the moment.

TABLE 4 Values of  $[\text{H}^+(\text{aq})]$ , with corresponding values of

$$\log \left\{ \frac{[\text{H}^+(\text{aq})]}{\text{mol l}^{-1}} \right\} \text{ and pH (at } 25^\circ\text{C})$$

$[\text{H}^+(\text{aq})]/\text{mol l}^{-1}$	$\log \left\{ \frac{[\text{H}^+(\text{aq})]}{\text{mol l}^{-1}} \right\}$	pH	
$10^1$ or 10	1	-1	
$10^0$ or 1	0	0	
$10^{-1}$ or 0.1	-1	+1	
$10^{-2}$ or 0.01	-2	+2	
$10^{-3}$ or 0.001	-3	+3	
$10^{-4}$ or 0.0001	-4		
$10^{-5}$ or 0.00001	-5		
$10^{-6}$ or 0.000001	-6		
$10^{-7}$ or 0.0000001	-7		
$10^{-8}$ or 0.00000001	-8		
$10^{-9}$ or 0.000000001	-9		
$10^{-10}$ or 0.0000000001	-10		
$10^{-11}$ or 0.00000000001	-11		
$10^{-12}$ or 0.000000000001	-12		
$10^{-13}$ or 0.0000000000001	-13		
$10^{-14}$ or 0.00000000000001	-14		

- In ITQ 10 you found that  $\log 4 = 0.6021$ . Does this value seem reasonable when compared with the values of  $\log 1$  and  $\log 10$  in Table 4?
- Well, 4 is a number between 1 and 10, so according to Table 4,  $\log 4$  should lie between 0 and 1: it does.

But the values in Table 4 indicate that for the concentration range of interest the logarithm itself will almost invariably be a negative number. For this reason, a widely used scale is defined in terms of the *negative* of the logarithm. This arbitrary, but useful, scale is called the **pH scale**:

$$\text{pH} = -\log \left\{ \frac{[\text{H}^+(\text{aq})]}{\text{mol l}^{-1}} \right\}$$

(39)

- Fill in the missing pH values in Table 4. What are the pH values of pure water and of human blood at  $25^\circ\text{C}$  ( $[\text{H}^+(\text{aq})] = 4.0 \times 10^{-8} \text{ mol l}^{-1}$ , as given in ITQ 10)?

- For pure water  $[\text{H}^+(\text{aq})] = 10^{-7} \text{ mol l}^{-1}$ , so

$$\log \left\{ \frac{[\text{H}^+(\text{aq})]}{\text{mol l}^{-1}} \right\} = -7.0 \text{ and the pH} = +7.0.$$

For human blood,

$$\begin{aligned} \log \left\{ \frac{[\text{H}^+(\text{aq})]}{\text{mol l}^{-1}} \right\} &= \log (4.0 \times 10^{-8}) \\ &= \log (4.0) + \log (10^{-8}) \\ &= (0.6021 - 8.0000) = -7.3979. \end{aligned}$$

So  $\text{pH} = +7.4$  (to two significant figures).

Further examples of this type of calculation are provided in ITQ 11 and in the SAQs at the end of Section 6. For the moment, try to familiarize your-

self with the pH scale by studying Table 4. Marked against the figures are the acidic and basic regions of the scale. You will remember from Section 6.1 that acidic solutions have  $[\text{H}^+(\text{aq})]$  greater than  $10^{-7}\text{ mol l}^{-1}$ , so their pH is less than 7. Conversely, basic solutions have pH greater than 7. To give you a better feel for pH, values of pH for some common chemical, natural, and household solutions are given in Table 5.

TABLE 5 pH values for some common solutions

Solution	pH
hydrochloric acid ( $0.1\text{ mol l}^{-1}$ )	1.0
gastric juice (human)	1.0–2.5
lemon juice	about 2.1
acetic acid ( $0.1\text{ mol l}^{-1}$ )*	2.9
orange juice	about 3.0
tomato juice	about 4.1
urine	6.0
rainwater (unpolluted)	5.2–6.5
saliva (human)	6.8
milk	about 6.9
pure water ( $25^\circ\text{C}$ )	7.0
blood (human)	7.4
seawater	7.9–8.3
ammonia ( $0.1\text{ mol l}^{-1}$ )†	11.1
sodium hydroxide ( $0.1\text{ mol l}^{-1}$ )	13.0

\* Approximately the concentration of household vinegar.

† Approximately the concentration of household ammonia solutions.

There are instruments called pH meters, which can be used to measure the pH of a given solution directly: many of the values in Table 5 were obtained in this way.

**ITQ 11** Consider the numbers 1, 0.1, 0.01 and 0.000 001.

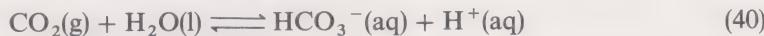
- (i) Write each of them in the form  $10^n$ , where  $n$  is an integer.
- (ii) Write down the logarithm to the base 10 of each number.
- (iii) What is the pH of the solutions in which  $[\text{H}^+(\text{aq})]$  is  $1\text{ mol l}^{-1}$ ,  $0.1\text{ mol l}^{-1}$  and  $0.000\ 001\text{ mol l}^{-1}$ , respectively?

**ITQ 12** Look at the entries in Table 5. Which is more acidic: orange juice or tomato juice? Vinegar or gastric juice? Blood or seawater?

### 6.3 ACID RAIN

In Experiment 1, you showed that carbon dioxide, a gas that you breathe out, dissolves in water to give a slightly acid solution:

- What reaction is responsible for the acidity?
- From Section 2.4, it is the equilibrium

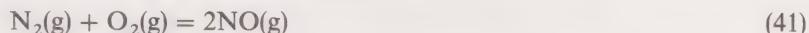


Carbon dioxide comprises about 0.3% of the Earth's atmosphere. Table 5 shows that unpolluted rainwater has a pH in the range 5.2–6.5. This slight acidity is explained by dissolved carbon dioxide that has undergone the reaction in Equation 40.

The acidity of  $\text{CO}_2$  solutions can be set in a more general context. Two points are worth making. First,  $\text{CO}_2$  is the oxide of a non-metallic element, carbon, and if they are significantly soluble in water, the oxides of non-metals always give acid solutions. By contrast, the oxides of metals may be either

bases ( $\text{MgO}$  in SAQ 4) or acids ( $\text{CrO}_3$  whose acid solution you will study at Summer School). Secondly, an element sometimes forms more than one normal oxide. Where this is so, *the higher oxide is always the more acidic*.

Rainwater is only slightly acid because Equilibrium 40 lies well over to the left:  $\text{CO}_2$  is a weak acid. But modern industrial economies generate other non-metallic oxides, which can increase the acidity of rainwater if they are discharged into the atmosphere. The problem can be traced back to two chemical culprits. First, sulphur compounds in coal and oil are converted into sulphur dioxide gas,  $\text{SO}_2$ , when the fuel is burnt in power stations. Secondly, spark temperatures in a car engine can exceed  $2000^\circ\text{C}$ , and at these high temperatures, some atmospheric nitrogen and oxygen can combine to form gaseous nitric oxide,  $\text{NO}$ :

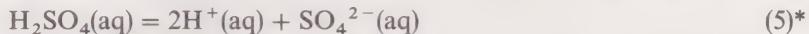


Up to 0.4% of the exhaust gases from an accelerating motor car can consist of nitric oxide. Substantial amounts are also produced in power stations.

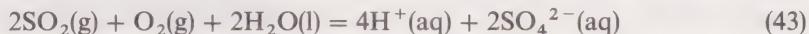
The acidity of  $\text{NO}$  is negligible, and that of  $\text{SO}_2$  is only weak. But both compounds can react with other atmospheric gases to form higher oxides of nitrogen and sulphur, whose solutions are therefore much more acidic. The details of these reactions are complicated. There are a number of steps, and other chemicals such as ozone and certain peroxides are produced and consumed. However, the *net results* are fairly easy to describe. Sulphur dioxide takes on atmospheric oxygen to give the trioxide:



$\text{SO}_3$  reacts with water vapour to give sulphuric acid,  $\text{H}_2\text{SO}_4$ , a strong acid like  $\text{HCl}$  and  $\text{HNO}_3$ . When dissolved in rainwater,  $\text{H}_2\text{SO}_4$  is completely dissociated, principally into  $\text{H}^+(\text{aq})$  and sulphate ions,  $\text{SO}_4^{2-}(\text{aq})$ :



The overall reaction is, therefore,



In a similar fashion, nitric oxide can be converted into nitric acid, which then dissolves in rainwater. The overall reaction is



Since 1950,  $\text{SO}_2$  and  $\text{NO}$  emissions in Europe have approximately doubled, and the acidity of rainwater has increased. On 10 April 1974, a rainstorm at Pitlochry in Scotland had a pH of 2.4, an acidity greater than that of vinegar, but that was exceptional. More typical are the data in Table 6, which compare rainwater compositions from similar sites in inland Scandinavia during the 1950s and 1970s. Data from a polluted site in the United States are also included.

TABLE 6 Ion concentrations and pH of rainwater from Scandinavian and US sites in 1956 and 1974

Site	pH	$[\text{H}^+(\text{aq})]$ $10^{-6} \text{ mol l}^{-1}$	$[\text{SO}_4^{2-}(\text{aq})]$ $10^{-6} \text{ mol l}^{-1}$	$[\text{NO}_3^-(\text{aq})]$ $10^{-6} \text{ mol l}^{-1}$	$[\text{HCO}_3^-(\text{aq})]$ $10^{-6} \text{ mol l}^{-1}$
inland Scandinavia (1956)	5.4	4	15	0	6
inland Scandinavia (1974)	4.3	48	26	26	0
inland north- eastern United States (1974)	3.9	114	55	50	0

## ACID RAIN

- How do these data corroborate our explanation of the origins of acid rain?
- Higher acidity and lower pH are associated with high concentrations of sulphate and nitrate, the ions produced alongside  $\text{H}^+(\text{aq})$  in Equations 43 and 44.

Figure 7 shows average pH contours for western European rain between 1978 and 1982. The low of 4.1 hovers over central Europe.

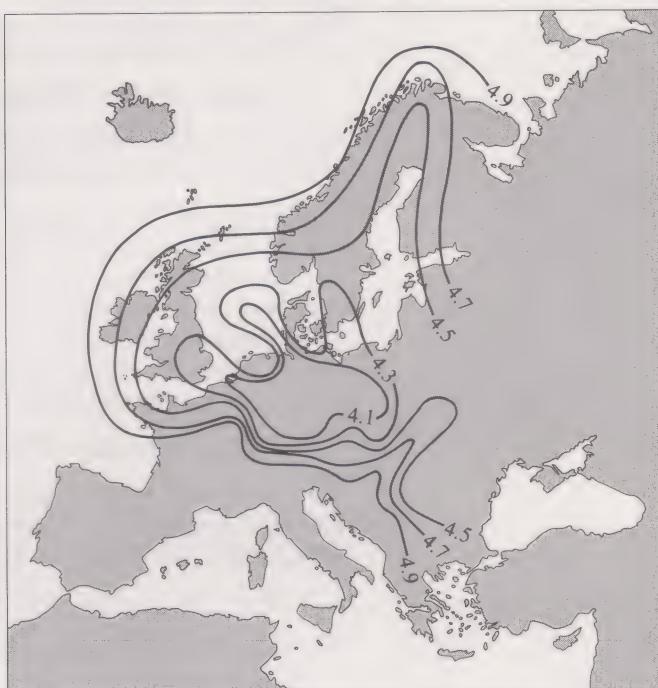


FIGURE 7 Mean pH values for rainfall over western Europe in the period 1978–82.

**Acid rain** is a political issue because those regions responsible for it are not always the chief sufferers. Tall stacks on power stations (Figure 8) may well export the problem sometimes as far as other countries. In Europe, the prevailing winds have a northerly drift and converge on Scandinavia. Thus, it has been estimated that only 8% of the sulphate falling on Norway is due to the activities of Norwegians, and that 17% comes from the UK. By contrast 79% of UK sulphate deposition is of British origin, and none is Norwegian.

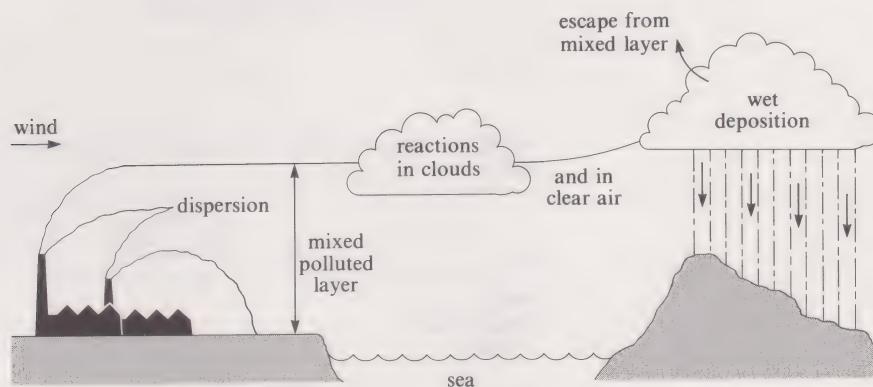
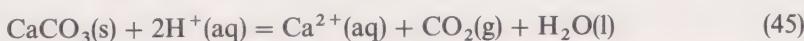


FIGURE 8 Dispersion of pollutants such as  $\text{SO}_2$  and  $\text{NO}$  leading subsequently to acid rain.

The vulnerability of different regions also varies widely. What is important is the capacity of the environment to neutralize the acidity after the rain touches ground. Land containing forms of calcium carbonate, such as chalk or limestone, is effective in this role because of the reaction with acid that is quoted in the answer to ITQ 1:



Unfortunately, the bedrock of Scandinavia consists mainly of rocks, such as granite or quartz sandstone, that are poor neutralizers of acidity. In such an environment, the impact of acid rain is likely to be more severe.

During the past 50 years, trout and salmon have disappeared from some 2000 lakes in southern Scandinavia. The influence of acid rain on something as complicated as the countryside is very difficult to assess, and wild and unsubstantiated claims have been made. However, there is strong evidence that acid rain is responsible for this particular catastrophe. Norway and Sweden have called for a reduction of SO<sub>2</sub> and NO emissions throughout Europe. In 1986, the UK government announced projected expenditure of £600 million on chemical plant to cut down the SO<sub>2</sub> in power station emissions, and to convert the gas into a marketable product, which will be calcium sulphate, sulphuric acid or sulphur. This action was judged inadequate by the Norwegian government.

## SUMMARY OF SECTION 6

1 Pure water contains tiny amounts of aqueous hydrogen and hydroxide ions.

2 The ion product of water

$$K_w = [H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14} \text{ mol}^2 \text{l}^{-2} \text{ at } 25^\circ\text{C}$$

controls the concentrations of hydrogen and hydroxide ions that can coexist in *any* aqueous solution. If either [H<sup>+</sup>(aq)] or [OH<sup>-</sup>(aq)] is known, the constant value of K<sub>w</sub> allows the other to be calculated.

3 The concentration of aqueous hydrogen ions in a solution can be expressed by stating its pH, which is defined as

$$\text{pH} = -\log \left\{ \frac{[H^+(aq)]}{\text{mol l}^{-1}} \right\}$$

4 The combustion of fossil fuels in power stations and motor vehicles produces the oxides SO<sub>2</sub> and NO. These react with atmospheric oxygen to form more acidic substances, such as sulphuric and nitric acid, which dissolve in rainwater and yield acid rain.

**SAQ 13** In Section 6.1, we said that in pure water at 25 °C, the ratio of ionized to un-ionized water molecules is about one to every thousand million. Confirm this by calculating a more accurate value from the concentrations worked out in Section 6.1.

**SAQ 14** 0.001 mole of nitric acid is dissolved in 10 litres of water at 25 °C. Calculate the hydrogen ion concentration, [H<sup>+</sup>(aq)], the pH, and the hydroxide ion concentration, [OH<sup>-</sup>(aq)], of the resulting solution.

**SAQ 15** The solubility of Ca(OH)<sub>2</sub> in water is 0.020 mol l<sup>-1</sup> at 25 °C. Calculate

- (i) The value of [OH<sup>-</sup>(aq)] in the saturated solution of Ca(OH)<sub>2</sub> at 25 °C;
- (ii) The corresponding value of [H<sup>+</sup>(aq)], given that K<sub>w</sub>, the ion product of water, is 1.0 × 10<sup>-14</sup> mol<sup>2</sup> l<sup>-2</sup>;
- (iii) The pH of the saturated solution at 25 °C.

**SAQ 16** Chlorine forms the oxides Cl<sub>2</sub>O and Cl<sub>2</sub>O<sub>7</sub>, which, on reaction with water, yield the acids HClO and HClO<sub>4</sub>, respectively. One of these acids is strong, like nitric acid, and the other is weak, even weaker than acetic acid.

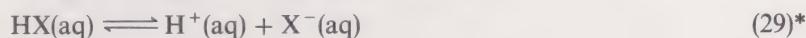
- (i) By inspecting the formulae of the oxides, decide which one reacts with water to form the strong acid. Write an equation for this reaction with water.
- (ii) Which acid is the weak one of the two? Write an equation for its dissociation in aqueous solution.

**SAQ 17** 0.0572 mole of pure acetic acid is dissolved in a little water, and more water is then added until the total volume of the solution is one litre. The pH of the solution is then measured with a pH meter, and found to be 3.00.

- Calculate a value of the acid dissociation constant  $K_a$ , and compare it with the value of Table 3.
- What is the ratio of un-ionized to ionized acetic acid molecules in the solution?

## 7 GENERALIZED FORM OF THE EQUILIBRIUM CONSTANT

Any chemical equilibrium at constant temperature has an equilibrium constant that provides a precise numerical relationship between the concentrations of the ingredients of the equilibrium system. In Sections 5 to 6.2, we illustrated this with equilibria of the general type



for which the equilibrium constant is

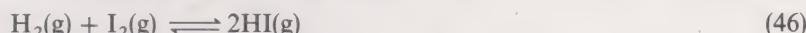
$$K = \frac{[\text{H}^+(\text{aq})][\text{X}^-(\text{aq})]}{[\text{HX(aq)}]} \quad (30)^*$$

These illustrative examples were of a very particular kind. First, all species in the equilibria are in aqueous solution. Secondly, the numbers preceding the formulae in the equations are all equal to one. Thus, *one* HX(aq) molecule breaks up into *one* H<sup>+</sup>(aq) ion and *one* X<sup>-</sup>(aq) ion. So what form does an equilibrium constant take when we break free of these narrow restrictions?

Consider one of the examples from Section 1: a mixture of hydrogen and iodine is heated in a sealed vessel at 427 °C. The purple colour of the iodine vapour decreases in intensity as the hydrogen and iodine react to form a colourless gas, hydrogen iodide, HI:



Eventually, there is no further change in the intensity of the colour: equilibrium has been reached. Although hydrogen and iodine molecules are still reacting together to form hydrogen iodide, this forward reaction is exactly balanced by hydrogen iodide molecules decomposing. We can now describe the system with the equilibrium equation



Notice how this example violates both of our previous restrictions. First, one formula in the equilibrium equation, that of HI, is preceded by a 2. Secondly, all the species in the equilibrium are gases. Note, however, that at equilibrium some definite number of moles of each gas will be present, and that the bulb will have a definite volume of, say, V litres. Each gas will be evenly dispersed throughout the bulb, so we can assign to it an equilibrium concentration in mol l<sup>-1</sup>, which is obtained by dividing the number of moles by V.

What is the numerical relationship between these equilibrium concentrations? It is supplied by the equilibrium constant, K, of Equation 46, which takes the form

$$K = \frac{[\text{HI(g)}]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} \quad (47)$$

At 427 °C, experiments show that K is close to 54.

Look carefully at Equation 47. Unlike Equation 30, it refers to a chemical equation, Equation 46, in which one of the formulae is preceded by a 2.

How does this 2 display its presence in Equations 46 and 47?

■ In Equation 46, it precedes the formula of  $\text{HI(g)}$ . In Equation 47, it becomes a power to which the concentration of  $\text{HI(g)}$  is raised.

To reinforce this point, recall our observation in Section 5: we noted that the equilibrium constant for Equation 25 could be obtained by multiplying the concentrations of the chemicals on the right-hand side together, and then dividing by the product of the concentrations of the chemicals on the left-hand side. If equation 46 is written,



this same procedure yields Equation 47.

With these insights, you can see that Equations 30 and 47 are particular examples of a general case. Suppose reactants A, B, ... etc. yield products P, Q, ... etc. in a reaction that reaches equilibrium:



Here,  $a$ ,  $b$ ,  $p$ ,  $q$  are the numbers used to balance the equation. Then the equilibrium constant takes the form,

$$K = \frac{[\text{P}]^p [\text{Q}]^q \dots}{[\text{A}]^a [\text{B}]^b \dots} \quad (50)$$

Notice that the concentration of each ingredient in Equation 50 is raised to a power equal to the number that precedes the ingredient in Equation 49. Thus adjusted, the concentrations of the products are multiplied together in the numerator of the equilibrium constant; those of the reactants are multiplied in the denominator.

During this procedure, the chemical Equation 49 fathers the equilibrium constant in Equation 50: until the first is specified, the second cannot be written down. *Any expression for an equilibrium constant is inextricably tied to a particular chemical equation from which it is derived.*

You will find an example that emphasizes this point in parts (c) and (d) of the following ITQ.

**ITQ 13** Write down expressions for the equilibrium constants of the following reactions:

- (a)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
- (b)  $\text{Sn}^{2+}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq}) \rightleftharpoons \text{Sn}^{4+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$
- (c)  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$
- (d)  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$

Because product concentrations appear in the numerators of equilibrium constants, and reactant concentrations in the denominators,  $K$  is large when, at equilibrium, the products in the parent equation are plentiful, and reactants are scarce. For this reason,  $K$  is a measure of the extent of reaction—of how far the reaction can proceed in a left to right direction when pure reactants are mixed and maintained at the temperature in question. Two extreme cases are supplied by two reactions in ITQ 13:



For the first reaction,  $K$  is very large: evidently equilibrium lies far over to the right-hand side, and the reaction should be effectively complete when equilibrium is attained. By contrast,  $K$  for the second reaction is tiny: you would expect a vanishingly small amount of product to be present at equilibrium. This point was made in Section 5.1 with reference to a specific type of reaction: the dissociation of an acid. Here it has been applied to reactions in general. This generalization of things learnt in Section 5 is also an important feature of SAQs 18 to 20, which you should now try.

## SUMMARY OF SECTION 7

1 The equilibrium constant of the general equilibrium,



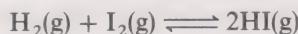
is given by

$$K = \frac{[P]^p [Q]^q \dots}{[A]^a [B]^b \dots} \quad (50)^*$$

Thus the expression for the equilibrium constant depends crucially on the form of the balanced equation that is used to describe the equilibrium.

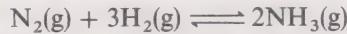
2 The size of the equilibrium constant at a particular temperature is a measure of how far the reaction will have gone when equilibrium is attained at that temperature. In other words, it indicates the equilibrium yield of the reaction at that temperature.

**SAQ 18** In Section 7, you were told that, at 427 °C, the equilibrium constant of the reaction



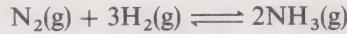
is about 54. In Section 1, you were told of an equilibrium mixture for this system which contained 0.35 mole of H<sub>2</sub>(g), 0.15 mole of I<sub>2</sub>(g) and 1.70 moles of HI(g) in a sealed bulb at 427 °C. Show that this composition is consistent with the equilibrium constant. Assume that the volume of the bulb is 1 litre.

**SAQ 19** Write down an expression for the equilibrium constant of the reaction mentioned in SAQ 8, namely



Use this expression to predict the effect of removing NH<sub>3</sub> from an equilibrium mixture by dissolving it in water. How does this compare with the predictions derived from Le Chatelier's principle?

**SAQ 20** At 25 °C, the equilibrium constant, K, of the reaction,



is  $2.70 \times 10^8 \text{ mol}^{-2} \text{ l}^2$ . A steel bulb of volume 1 litre contains 0.0100 mole of H<sub>2</sub>(g) and 0.0033 mole of N<sub>2</sub>(g) at 25 °C. Assuming that the gases are then in equilibrium with ammonia:

- (i) How many moles of ammonia does the bulb contain?
- (ii) If the equilibrium state was set up by pumping N<sub>2</sub>(g) and H<sub>2</sub>(g) into the empty bulb, and then allowing them to reach equilibrium, how many moles of N<sub>2</sub>(g) and of H<sub>2</sub>(g) were pumped in?

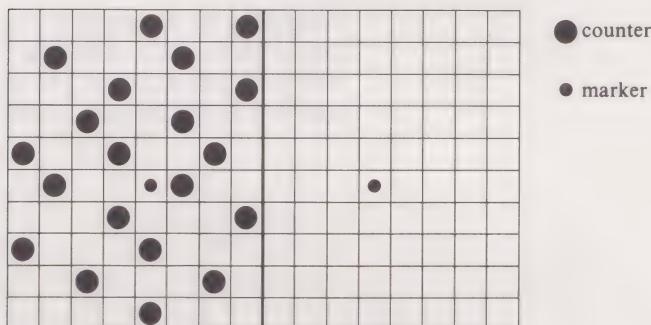
## 8 TV NOTES: EQUILIBRIUM RULES—OK?

The key points in the programme are summarized below.

1 A pH meter (an instrument that you will use at Summer School) was used to show that a typical weak acid, acetic acid ( $\text{HAc}$ ), is only partly dissociated into ions in solution; a dynamic equilibrium is set up:

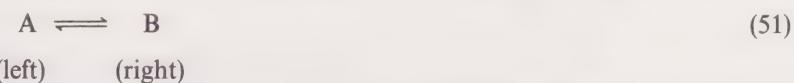


2 The idea of a dynamic equilibrium was examined with the help of a simple analogy—our ‘equilibrium game’. If you would like to try it at home, you will need the equipment illustrated in Figure 9. The ‘rules of the game’ simply involve deciding how many squares the ‘marker’ on each side is allowed to move in any one turn: we chose two for the left-hand player and three for the right-hand one. Why not try some different values and see if you can predict what will happen?



**FIGURE 9** Equipment for the ‘equilibrium game’. The size of the board is not critical, but it should be divided into two equal parts. We used 20 counters.

The main object of the game was to show that it is possible to build up and maintain a roughly constant distribution of counters between the two players, even though individual counters are still going back and forth. But the analogy should not be taken too far. Strictly speaking, the game should only be compared with a simple equilibrium between two species:

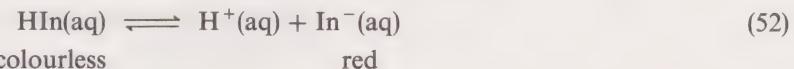


Even here, there are problems. The reactant and product in a chemical system are not in separate compartments; neither is there a marker that ‘magically’ converts one into the other!

Despite these reservations, you saw that our artificial equilibrium responded to a disturbance (removal of all the counters from the right-hand side) in much the same way as a chemical system: there was a net movement from left to right until a new equilibrium was established.

3 We used these ideas to interpret the observed effects of disturbing two chemical systems. Adding acetate ions to an acetic acid solution shifted the equilibrium in Equation 25 to the left, as shown by a marked fall in the concentration of  $\text{H}^+(\text{aq})$ . Compare the exercises in ITQ 7.

We then showed that Ian Soutar’s splendid trick revolves around the manipulation of the following simple equilibrium:



where HIn represents an indicator (phenolphthalein). The equilibrium was shifted back and forth (and hence the colour of the solution changed) by adjusting the concentration of  $\text{H}^+(\text{aq})$ .

These effects are summarized by Le Chatelier’s principle.

4 The final part of the programme introduced an experimental technique that you will use at Summer School—absorption spectrophotometry. You saw how this technique can, in principle, be used to determine the equilibrium constant  $K$  for a second indicator, bromophenol blue:



where

$$K = \frac{[\text{H}^+(\text{aq})][\text{In}^-(\text{aq})]}{[\text{HIn(aq)}]}$$

As you saw, the technique depends on the fact that both forms of the indicator ( $\text{HIn}$  and  $\text{In}^-$ ) absorb light, but in different regions of the visible spectrum (Figure 10). Thus, for example, the purple solution of  $\text{In}^-$  absorbs light mainly between 500 nm and 620 nm—the green, yellow and orange region. The transmitted light, which is what we see, corresponds to a mixture of the remaining blues and red.

When will the purple form predominate?

According to the equilibrium in Equation 53, the balance between the coloured forms again depends on the concentration of  $\text{H}^+(\text{aq})$ : thus,  $\text{In}^-(\text{aq})$  will predominate when  $[\text{H}^+(\text{aq})]$  is low, and vice versa. This is how we were able to record spectra of the two ‘pure’ species (Figure 10).

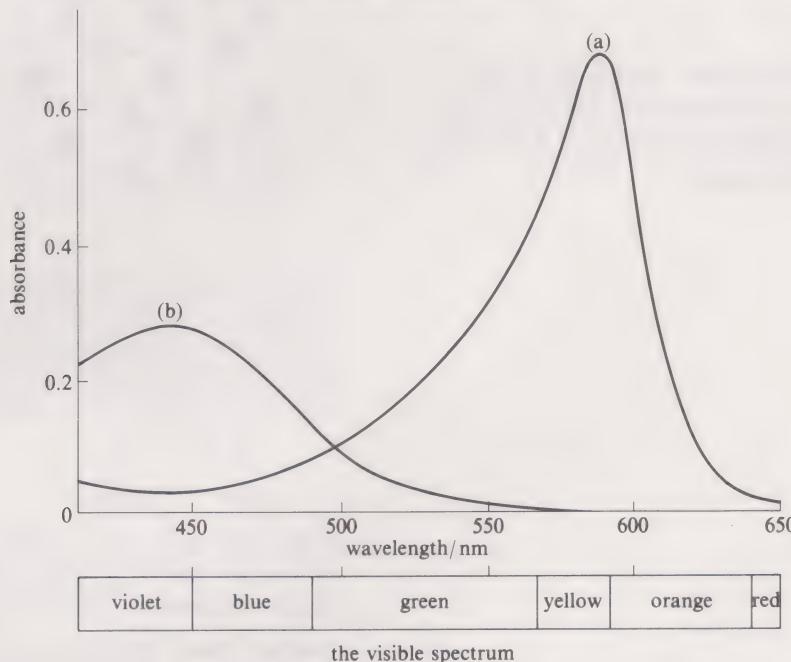


FIGURE 10 Absorption spectra of bromophenol blue related to the visible spectrum: (a) when  $[\text{H}^+(\text{aq})]$  is low,  $\text{In}^-(\text{aq})$  predominates; (b) when  $[\text{H}^+(\text{aq})]$  is high,  $\text{HIn(aq)}$  predominates.

You will see at Summer School how we can use such spectra to calculate the relative equilibrium concentrations of the two forms in a solution of intermediate pH that contains them both.

The values we obtained are given in Table 7, where the hydrogen ion concentration is expressed as the pH, as measured by a pH meter. When you have read about pH in Section 6.2, you should complete this Table and thus convince yourself that  $K$  is indeed close to a constant.

TABLE 7 Experimental results for the dissociation of bromophenol blue

pH	$[\text{H}^+(\text{aq})]/\text{mol l}^{-1}$	$[\text{In}^-(\text{aq})]/[\text{HIn(aq)}]$	$K/\text{mol l}^{-1}$
4.6		3.80	
4.3	$5.01 \times 10^{-5}$	1.77	$8.87 \times 10^{-5}$
3.6		0.33	

5 Finally, you saw that the equilibrium in Equation 54 can be shifted over to the right (the colour darkened) by raising the temperature



The equilibrium constant for this reaction is given by

$$K = \frac{[\text{NO}_2(\text{g})]^2}{[\text{N}_2\text{O}_4(\text{g})]}$$

If  $[\text{NO}_2(\text{g})]$  increases,  $[\text{N}_2\text{O}_4(\text{g})]$  must decrease (we did not add any material to the flask), which together imply that  $K$  must increase with increasing temperature. In other words, the value of  $K$  depends on the temperature. The reasons why this should be so are taken up in Section 6 of Unit 16.

## 9 UNIT SUMMARY AND A FORWARD LOOK

Two major subjects were introduced in this Unit: the concept of acids and bases, and the idea of chemical equilibrium. You saw that chemical reactions, if they occur at detectable speeds, can be said to be moving towards chemical equilibrium. In Sections 5 and 6, you were shown how an equilibrium position, at some fixed temperature, can be characterized by an equilibrium constant whose size gives us an idea of how far the reaction must go before equilibrium is reached.

The preceding paragraph contains two important qualifications. The second sentence implies that chemical equilibrium will *not* be reached if *the reaction does not proceed at a detectable speed*. In other words, extreme slowness of reaction can block the path to equilibrium. Such a problem was deliberately avoided in Unit 15. Indeed this was one reason why acids, bases, electrolytes and aqueous ions were so prominent. Studying the reactions of such substances, it is easy to be selective, and choose reactants that set off determinedly towards equilibrium when they are brought into contact! In Unit 16 however, we shall move away from such systems and this will force us to confront the question of *rates* of reaction more directly. From the problem of *how far* a reaction goes, we shall shift to the problem of *how fast* it goes as it moves towards equilibrium.

The second qualification in our first paragraph is the recognition that equilibrium constants must be defined at *some fixed temperature*. As noted in Section 4.1, this is necessary because equilibrium positions and, therefore, equilibrium constants, vary with temperature. For example, from Section 7, at 427 °C, the equilibrium constant of the reaction



is 54. However, at 227 °C it is 128, and at 627 °C it is 35. In some cases therefore, such as Reaction 46, the equilibrium constant decreases with increasing temperature; in other cases, such as Reaction 54, it increases. To an industrialist, anxious to obtain as much product as possible from an equilibrium system, the question of what determines such a change of yield with temperature is of great importance. This question is also answered in Unit 16, which is concerned with chemical energetics.

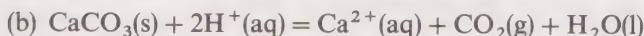
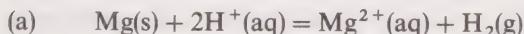
## OBJECTIVES FOR UNIT 15

After you have worked through this Unit, you should be able to:

- 1 Explain the meaning of, and use correctly, all the terms flagged in the text.
- 2 Recall the operational definitions of an acid and a base, and classify given substances accordingly. (*Experiment 1, ITQ 1, SAQs 1 and 4*).
- 3 Use the Arrhenius definitions of an acid and a base to interpret the reactions of acids and bases (*ITQs 1–3, SAQs 1–4*).
- 4 Calculate in moles per litre the concentration of a solution, or of the ions in a solution, given the mass of solute in a given volume of solution, appropriate relative atomic masses, and the dissolution reaction of the solute (*ITQs 4 and 5, SAQ 5*).
- 5 Use Le Chatelier's principle to predict the consequences of a change in the concentration of a constituent of a chemical equilibrium (*ITQs 6 and 7, SAQs 7 and 8*).
- 6 Given a list of strong electrolytes that are very sparingly soluble, identify pairs of strong electrolyte solutions that will produce precipitates when they are mixed (*SAQ 6*).
- 7 Write down the expressions for the equilibrium constants for the dissociation of a weak acid,  $K_a$ , and for the dissociation of water  $K_w$  (*ITQs 8 and 9, SAQs 10–15 and 17*).
- 8 Show how the consequences of change in the concentration of a constituent of a chemical equilibrium at constant temperature can be predicted from the requirement that the equilibrium constant is constant under these conditions (*ITQs 8 and 9, SAQ 19*).
- 9 Given appropriate concentrations, calculate unknown concentrations at equilibrium from equilibrium constants, and unknown equilibrium constants from concentrations (*SAQs 10–15, 17, 18 and 20*).
- 10 Distinguish the meanings of the words 'strength' and 'concentration', as applied to solutions of electrolytes (*SAQs 9, 12 and 16*).
- 11 Define the logarithm to the base 10 of a number and, when given a number that can be written as  $10^n$ , where  $n$  is a positive or negative integer, state what its logarithm to the base 10 is (*ITQs 10a and 11; SAQ 14*).
- 12 Use a pocket calculator to find the logarithms to the base 10 of a given number or product of numbers (*ITQs 10b and 10c; SAQ 15*).
- 13 Recognize that oxides of non-metals are usually acidic, and that higher oxides are more acidic than lower ones (*SAQ 16*).
- 14 Calculate the pH of a solution from either its hydrogen ion concentration or its hydroxide ion concentration, or interpret a given value of pH (*ITQs 10 and 11; SAQs 14, 15 and 17*).
- 15 Write down the equilibrium constant of a reaction that occurs in aqueous solution or the gas phase, given the balanced equation for the reaction (*ITQ 13; SAQs 18–20*).

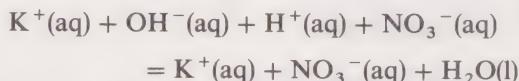
# ITQ ANSWERS AND COMMENTS

**ITQ 1** For the reaction of the given substances with an acid,  $\text{H}^+(\text{aq})$ :



Notice that although the total charge on each side of these equations is *not* zero, the equations are nevertheless balanced: the total charge on each side of the equation is the same (+ 2).

**ITQ 2** Aqueous solutions of KOH contain the ions  $\text{K}^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$ ; aqueous solutions of  $\text{HNO}_3$  contain the ions  $\text{H}^+(\text{aq})$  and  $\text{NO}_3^-(\text{aq})$ . By analogy with Equation 10, the reaction could be written



But  $\text{K}^+(\text{aq})$  and  $\text{NO}_3^-(\text{aq})$  occur on both sides so they can be eliminated to give



This is just Equation 11 again: at the level of ions and molecules, the reaction between KOH and  $\text{HNO}_3$  is identical with that between NaOH and HCl.

**ITQ 3** Potassium nitrate,  $\text{KNO}_3$ , which is a salt. When the reaction of ITQ 2 is over, the aqueous solution contains  $\text{K}^+(\text{aq})$ ,  $\text{NO}_3^-(\text{aq})$  and water. If the water evaporates, the solid left behind contains the potassium cation of the base KOH, and the nitrate anion of the acid  $\text{HNO}_3$ .

**ITQ 4**  $25 \text{ g l}^{-1}$ . Every  $200 \text{ cm}^3$  of solution contains 5 g of sugar, so a litre ( $1000 \text{ cm}^3$ ) of such a solution will contain 25 g of sugar.

**ITQ 5** With the molecular formula  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , one mole of sucrose has a mass (in grams) of

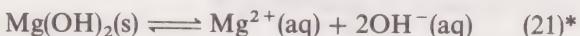
$$[(12 \times 12) + (22 \times 1) + (11 \times 16)] \text{ g} = 342 \text{ g}$$

Each litre of solution contains 25 g which is

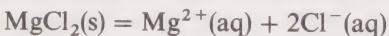
$$\frac{25}{342} \text{ mol} = 0.0731 \text{ mol}$$

Thus the concentration of the solution is 0.0731 mole per litre, i.e.  $0.0731 \text{ mol l}^{-1}$ .

**ITQ 6** The equilibrium system is again



If solid  $\text{MgCl}_2$  is dissolved in the solution, additional  $\text{Mg}^{2+}(\text{aq})$  is produced:



so the concentration of  $\text{Mg}^{2+}(\text{aq})$  is increased. This is an external constraint, which disturbs the equilibrium of Equation 21. According to Le Chatelier's principle, the system reacts so as to lessen the effect of the constraint, that is, so as to reduce the increased concentration of

$\text{Mg}^{2+}(\text{aq})$ . It can do this if the right to left reaction becomes predominant, resulting in a net transfer of  $\text{Mg}^{2+}(\text{aq})$  and  $\text{OH}^-(\text{aq})$  into  $\text{Mg(OH)}_2(\text{s})$ . This will lower the concentration of  $\text{OH}^-(\text{aq})$  below its original value. The lowering goes on until a new position of equilibrium is reached.

**ITQ 7** The equilibrium system is

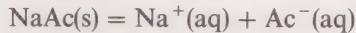


(i) When  $\text{NaOH(s)}$  is dissolved in the solution,  $\text{OH}^-(\text{aq})$  is produced, and then reacts with  $\text{H}^+(\text{aq})$ :



This lowering of the hydrogen ion concentration is an external constraint on Equilibrium 25. The system responds by trying to lessen the effect of the constraint, that is, to raise the reduced concentration of  $\text{H}^+(\text{aq})$ . The left to right reaction becomes predominant, and  $\text{HAc(aq)}$  is transformed into  $\text{H}^+(\text{aq})$  and  $\text{Ac}^-(\text{aq})$ . The characteristic smell of HAc is therefore diminished. Note that your solution of  $\text{NaAc(s)}$ , which contains much  $\text{Na}^+(\text{aq})$  and  $\text{Ac}^-(\text{aq})$ , is odourless:  $\text{Ac}^-(\text{aq})$  does not smell like HAc.

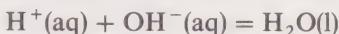
(ii) Sodium acetate is a salt, and is therefore a strong electrolyte:



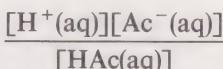
When dissolved in acetic acid, it increases the concentration of  $\text{Ac}^-(\text{aq})$ . The system of Equation 25 responds by trying to lower this increased concentration. The right to left reaction becomes dominant and  $\text{H}^+(\text{aq})$  combines with  $\text{Ac}^-(\text{aq})$  to form  $\text{HAc(aq)}$ . The hydrogen ion concentration therefore drops.

**ITQ 8** As noted in ITQ 7, the addition of sodium hydroxide results in the breakdown of undissociated HAc molecules and a consequent decrease in the smell of the solution.

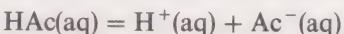
The  $\text{OH}^-(\text{aq})$  formed by dissociation of NaOH combines with  $\text{H}^+(\text{aq})$ :



This reduces the concentration of  $\text{H}^+(\text{aq})$ , which we write as  $[\text{H}^+(\text{aq})]$ , and therefore lowers the value of



below the *equilibrium* value of  $1.8 \times 10^{-5} \text{ mol l}^{-1}$  (at  $25^\circ\text{C}$ ). In order to return to equilibrium, the system must re-establish this value. The left to right process in Equilibrium 25 becomes dominant:



and some HAc molecules dissociate. The process continues until the consequent reduction in  $[\text{HAc(aq)}]$  and increase in  $[\text{Ac}^-(\text{aq})]$  and  $[\text{H}^+(\text{aq})]$  have increased the lowered value of the fraction back to  $1.8 \times 10^{-5} \text{ mol l}^{-1}$ .

**ITQ 9** Statements (a), (d) and (e) are correct; (b) and (c) are incorrect. The addition of  $\text{Ca}(\text{OH})_2$  raises  $[\text{OH}^-(\text{aq})]$ , but the product  $[\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$  must remain at the equilibrium value, so  $[\text{H}^+(\text{aq})]$  will decrease by the formation of more undissociated water:



The increase in the number of water molecules, however, is small compared with the number that are already present.  $K_w$  is a constant at constant temperature and so it does not change.

**ITQ 10** (a)  $10 = 10^1$  so  $\log 10 = 1$ ;  $100 = 10^2$  so  $\log 100 = 2$ ;  $0.001 = 10^{-3}$  so  $\log 0.001 = -3$ .

(b) Using your calculator,  $\log 4 = 0.6021$ ;  $\log 40 = 1.6021$ ;  $\log 0.4 = -0.3979$ .

Notice that

$$\begin{aligned}\log 40 &= \log (10 \times 4) \\ &= \log 10 + \log 4 \text{ (from Equation 38)} \\ &= 1 + 0.6021 \\ &= 1.6021\end{aligned}$$

and similarly,

$$\begin{aligned}\log 0.4 &= \log (4 \times 10^{-1}) \\ &= \log 4 + \log 10^{-1} \\ &= 0.6021 - 1 \\ &= -0.3979\end{aligned}$$

(c) The value is  $-7.4$ . If  $[\text{H}^+(\text{aq})] = 4 \times 10^{-8} \text{ mol l}^{-1}$

$$\begin{aligned}\log \left\{ \frac{[\text{H}^+(\text{aq})]}{\text{mol l}^{-1}} \right\} &= \log (4 \times 10^{-8}) \\ &= \log 4 + \log 10^{-8} \\ &= 0.6021 - 8 \\ &= -7.3979 \\ &= -7.4 \text{ (to two significant figures)}\end{aligned}$$

**ITQ 11** (i)  $10^0$ ,  $10^{-1}$ ,  $10^{-2}$  and  $10^{-6}$ , respectively; (ii) 0,  $-1$ ,  $-2$  and  $-6$ , respectively; (iii) 0, 1 and 6, respectively.

The answers to part (ii) are just the powers of 10 in part (i). Since  $\text{pH} = -\log ([\text{H}^+(\text{aq})]/\text{mol l}^{-1})$ , the answers in part (iii) are just minus those in part (ii).

**ITQ 12** Orange juice is more acidic than tomato juice; gastric juice is more acidic than vinegar; blood is more acidic than seawater. From the definition of pH, the lower the pH, the more acidic the solution.

**ITQ 13** Applying Equation 50:

$$(a) K = \frac{[\text{NO(g)}]^2}{[\text{N}_2(\text{g})][\text{O}_2(\text{g})]}$$

$$(b) K = \frac{[\text{Sn}^{4+}(\text{aq})][\text{Fe}^{2+}(\text{aq})]^2}{[\text{Sn}^{2+}(\text{aq})][\text{Fe}^{3+}(\text{aq})]^2}$$

$$(c) K = \frac{[\text{H}_2\text{O(g)}]^2}{[\text{H}_2(\text{g})]^2[\text{O}_2(\text{g})]}$$

$$(d) K = \frac{[\text{H}_2\text{O(g)}]}{[\text{H}_2(\text{g})][\text{O}_2(\text{g})]^{1/2}}$$

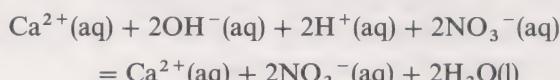
Note that for (c) and (d) the two values of  $K$  are different, even though they refer to the same reaction—the reaction of hydrogen with oxygen to give steam. This is because in (c) and (d), different balanced equations have been chosen to represent the same reaction, so different equilibrium constants result. This emphasizes the point immediately prior to ITQ 13.

In fact, the equilibrium constant in (c) is the square of that in (d), the experimental values at  $25^\circ\text{C}$  being  $33 \times 10^{80} \text{ mol}^{-1} \text{l}$  and  $5.74 \times 10^{40} \text{ mol}^{-1/2} \text{l}^{1/2}$ . The two expressions are completely equivalent and give exactly the same results for equilibrium concentrations.

## SAQ ANSWERS AND COMMENTS

**SAQ 1** (i) a; (ii) c, d; (iii) b; (iv) b; (v) a. You are referred to the text.

**SAQ 2** (i) Because the formula of calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , yields two hydroxide ions, and that of nitric acid,  $\text{HNO}_3$ , yields one hydrogen ion, each  $\text{Ca}(\text{OH})_2$  must react with two  $\text{HNO}_3$ . In an ionic form,



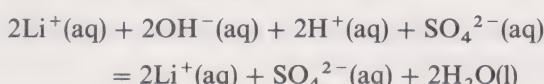
Eliminating the ions  $\text{Ca}^{2+}(\text{aq})$  and  $\text{NO}_3^-(\text{aq})$ , which are common to both sides, we get



This reduces to Equation 11 when divided through by 2.

(ii) By similar reasoning, two  $\text{LiOH}$  will be required to

react with each  $\text{H}_2\text{SO}_4$ . In an ionic form,



On elimination of  $\text{Li}^+(\text{aq})$  and  $\text{SO}_4^{2-}(\text{aq})$  and division by 2, Equation 11 again remains.

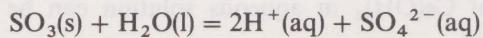
**SAQ 3** (i) Calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ ; (ii) lithium sulphate,  $\text{Li}_2\text{SO}_4$ . Combine the cation of the base with the anion of the acid in a ratio that produces electrical neutrality.

**SAQ 4** If  $\text{MgO}$  acts as a base, it must react with and dissolve in water to give some  $\text{OH}^-(\text{aq})$ . With the familiar  $\text{Mg}^{2+}(\text{aq})$  cation as the other likely product, we get



Likewise,  $\text{SO}_3$  must react with water to yield some

$\text{H}^+(\text{aq})$ . With the familiar sulphate anion as the other likely product, we get



**SAQ 5** (i)  $0.1 \text{ mol l}^{-1}$ ; (ii)  $0.2 \text{ mol l}^{-1}$ ; (iii)  $0.1 \text{ mol l}^{-1}$ .

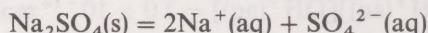
The molar mass of  $\text{Na}_2\text{SO}_4$  is

$$[(2 \times 23) + (1 \times 32) + (4 \times 16)] \text{ g} = 142 \text{ g}$$

The concentration of the solution is  $14.2 \text{ g l}^{-1}$ , which is equal to

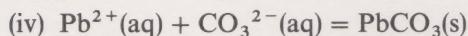
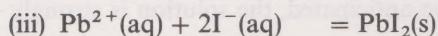
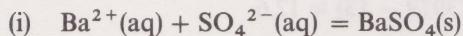
$$\frac{14.2}{142} \text{ mol l}^{-1} = 0.1 \text{ mol l}^{-1}$$

The equation for the dissociation is



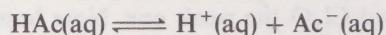
On dissolution therefore, the 0.1 mole of  $\text{Na}_2\text{SO}_4$  in each litre becomes 0.2 mole of  $\text{Na}^+(\text{aq})$  and 0.1 mole of  $\text{SO}_4^{2-}(\text{aq})$ .

**SAQ 6** (i) A white precipitate of barium sulphate,  $\text{BaSO}_4$ , appears. (ii) No visible reaction: the mixture is a clear colourless solution. (iii) A yellow precipitate of lead iodide,  $\text{PbI}_2$ , appears. (iv) A white precipitate of lead carbonate,  $\text{PbCO}_3$ , appears. The equations are



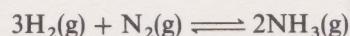
See Section 4.3. Answers are obtained by looking for combinations of cations and anions that might give very sparingly soluble compounds. In (ii), all such combinations of the ions  $\text{Ba}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  ( $\text{Ba}(\text{NO}_3)_2$ ,  $\text{BaCl}_2$ ,  $\text{NaCl}$ ,  $\text{NaNO}_3$ ) are soluble so there is no visible reaction. In the other cases, note that the ion combination that remains in solution is that of a soluble compound: (i)  $\text{NaCl}$ , (iii)  $\text{KNO}_3$ , (iv)  $\text{NaNO}_3$ .

**SAQ 7** The concentration of  $\text{Ac}^-(\text{aq})$  falls and that of  $\text{HAc}(\text{aq})$  rises. The equilibrium system is



$\text{HCl}$  is a strong electrolyte and, when it dissolves, it raises the concentration of  $\text{H}^+(\text{aq})$ . The system therefore reacts to lower this increased concentration:  $\text{Ac}^-(\text{aq})$  reacts with  $\text{H}^+(\text{aq})$  to form  $\text{HAc}(\text{aq})$ .

**SAQ 8** The balanced equation for the reaction is as follows:



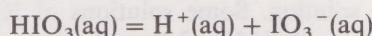
If an equilibrium mixture of  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{NH}_3$  is washed with a spray of water, much more  $\text{NH}_3$  will dissolve than  $\text{H}_2$  and  $\text{N}_2$ . Removing  $\text{NH}_3$  in this way constitutes an external constraint on the gaseous equilibrium. According to Le Chatelier's principle, the balance can be restored by further reaction of  $\text{N}_2$  and  $\text{H}_2$  to form  $\text{NH}_3$ : in qualitative terms, the equilibrium will be shifted to the right and more ammonia will be formed.

**SAQ 9** (i) d; (ii) a; (iii) c; (iv) b; (v) d.

See Section 4.5. From Section 4.2, a saturated solution of  $\text{Mg}(\text{OH})_2$  is very dilute, but as noted in Section 4.5, all dissolved  $\text{Mg}(\text{OH})_2$  forms ions. In example (iv), sugar would be better described as a non-electrolyte: unlike acetic acid, any dissociation is negligible. In example (v), potassium iodide is freely soluble in water (Table 2), so a saturated solution will be concentrated. It is also a salt, and all salts are strong electrolytes.

**SAQ 10** (i)  $[\text{H}^+(\text{aq})] = [\text{IO}_3^-(\text{aq})] = 0.41 \text{ mol l}^{-1}$ ; (ii) 29%.

The acid dissociates thus:



and, from Table 3, the acid dissociation constant,  $K_a$ , is,

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{IO}_3^-(\text{aq})]}{[\text{HIO}_3(\text{aq})]} = 0.17 \text{ mol l}^{-1}$$

The acid is added to water until  $[\text{HIO}_3(\text{aq})] = 1 \text{ mol l}^{-1}$ . Those molecules that have dissociated have yielded equal numbers of the ions  $\text{H}^+(\text{aq})$  and  $\text{IO}_3^-(\text{aq})$ , so

$$[\text{H}^+(\text{aq})] = [\text{IO}_3^-(\text{aq})]$$

Therefore,

$$\frac{[\text{IO}_3^-(\text{aq})]^2}{1 \text{ mol l}^{-1}} = 0.17 \text{ mol l}^{-1}$$

$$[\text{IO}_3^-(\text{aq})]^2 = 0.17 \text{ mol}^2 \text{l}^{-2}$$

$$[\text{IO}_3^-(\text{aq})] = 0.41 \text{ mol l}^{-1}$$

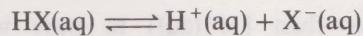
Thus, of the total acid added to each litre of solution, 1 mole remains undissociated, and 0.41 mole has dissociated. That is, 1.41 moles were added to each litre, of which 0.41 mole, or 29%, is dissociated into ions.

Note that the percentage of dissociation is much greater than in the analogous example of acetic acid in Section 5.1. This is because  $K_a$  is much greater.

**SAQ 11**

$[\text{HX}(\text{aq})] = [\text{H}^+(\text{aq})] = [\text{X}^-(\text{aq})] = 0.05 \text{ mol l}^{-1}$ ;  $K_a = 0.05 \text{ mol l}^{-1}$ .

The dissociation equilibrium is



If the total concentration of dissolved acid is  $0.1 \text{ mol l}^{-1}$ , and half of the acid molecules remain undissoiated in the solution, then  $[\text{HX}(\text{aq})] = 0.05 \text{ mol l}^{-1}$ . The other half of the acid molecules break down into equal numbers of  $\text{H}^+(\text{aq})$  and  $\text{X}^-(\text{aq})$  ions, so  $[\text{H}^+(\text{aq})] = [\text{X}^-(\text{aq})] = 0.05 \text{ mol l}^{-1}$ . The acid dissociation constant is then obtained as:

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{X}^-(\text{aq})]}{[\text{HX}(\text{aq})]} \\ = \frac{(0.05 \text{ mol l}^{-1}) \times (0.05 \text{ mol l}^{-1})}{0.05 \text{ mol l}^{-1}} \\ = 0.05 \text{ mol l}^{-1}$$

From Table 3,  $K_a$  for  $\text{HNO}_2(\text{aq})$  is  $4.5 \times 10^{-4} \text{ mol l}^{-1}$  or  $0.00045 \text{ mol l}^{-1}$ , that is, much smaller than  $0.05 \text{ mol l}^{-1}$ . This suggests that in a solution of  $\text{HNO}_2$  of concentration  $0.1 \text{ mol l}^{-1}$ , a lot more than half the dissolved acid must be in an undissociated state.

**SAQ 12** Only (a) is correct.

In aqueous solution,  $\text{HNO}_3$  is completely dissociated into ions. As this is not true of solutions of  $\text{HNO}_2$  (SAQ 11), this must mean that  $\text{HNO}_3$  is the stronger acid, so (b) is incorrect. This is true whatever concentrations of the two acids are being compared, because acid strength is related to the proportion of total acid that dissociates, not to the total concentration, or even to the concentration of  $\text{H}^+(\text{aq})$  in solution. Some solutions of  $\text{HNO}_2$  will have larger values of  $[\text{H}^+(\text{aq})]$  than some containing very much lower concentrations of  $\text{HNO}_3$ , but statement (b) is always incorrect.

In this case the  $\text{HNO}_2$  is twice as concentrated as the  $\text{HNO}_3$  but, as you found in SAQ 11, well over half the  $\text{HNO}_2$  is undissociated. This means that  $[\text{H}^+(\text{aq})]$  must be greater in the  $\text{HNO}_3$  solution, so (c) is incorrect.

**SAQ 13** A more accurate figure is one in 560 million. In Section 6.1, the concentration of water molecules in pure water *assuming no ionization* is calculated to be  $55.6 \text{ mol l}^{-1}$ , and  $[\text{H}^+(\text{aq})] = 1 \times 10^{-7} \text{ mol l}^{-1}$ . Every water molecule that ionizes produces one  $\text{H}^+(\text{aq})$ , so

$$[\text{ionized H}_2\text{O}] = [\text{H}^+(\text{aq})] = 1.0 \times 10^{-7} \text{ mol l}^{-1}$$

The concentration of ionized water molecules is thus negligible when compared with  $55.6 \text{ mol l}^{-1}$ , so the latter figure will serve for the concentration of water molecules left un-ionized. Thus in one litre there are 55.6 moles of un-ionized and  $1.0 \times 10^{-7}$  mole of ionized water molecules: the ratio is 560 million (to two significant figures).

**SAQ 14**  $[\text{H}^+(\text{aq})] = 1.0 \times 10^{-4} \text{ mol l}^{-1}$ ;  $\text{pH} = 4$ ;  $[\text{OH}^-(\text{aq})] = 1.0 \times 10^{-10} \text{ mol l}^{-1}$ .

Nitric acid is strong, and every mole dissociates to give one mole of  $[\text{H}^+(\text{aq})]$ . Assuming that the final volume of the solution is 10 litres, the dissociation of the  $\text{HNO}_3$  yields

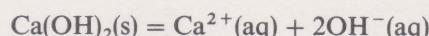
$$[\text{H}^+(\text{aq})] = \frac{0.001 \text{ mol}}{101} = 1.0 \times 10^{-4} \text{ mol l}^{-1}$$

This is far greater than  $[\text{H}^+(\text{aq})]$  in pure water ( $10^{-7} \text{ mol l}^{-1}$ ), so we can ignore any contribution from the solvent and take it to be the real value of  $[\text{H}^+(\text{aq})]$ . Then  $\text{pH} = -\log[10^{-4}] = -(-4) = 4$ . Using the ion product of water,

$$\begin{aligned} [\text{OH}^-(\text{aq})] &= \frac{1.0 \times 10^{-14} \text{ mol}^2 \text{l}^{-2}}{[\text{H}^+(\text{aq})]} \\ &= \frac{1.0 \times 10^{-14} \text{ mol}^2 \text{l}^{-2}}{1 \times 10^{-4} \text{ mol l}^{-1}} \\ &= 1.0 \times 10^{-10} \text{ mol l}^{-1} \end{aligned}$$

**SAQ 15** (i)  $[\text{OH}^-(\text{aq})] = 0.040 \text{ mol l}^{-1}$ ; (ii)  $[\text{H}^+(\text{aq})] = 2.5 \times 10^{-13} \text{ mol l}^{-1}$ ; (iii)  $\text{pH} = 12.6$ .

First, recall that the solubility of a solid represents the concentration of the saturated solution. The dissociation of  $\text{Ca}(\text{OH})_2$  in aqueous solution can be represented as



Assuming that all dissolved material is in the form of  $\text{Ca}^{2+}(\text{aq})$  and  $\text{OH}^-(\text{aq})$  ions, that is that  $\text{Ca}(\text{OH})_2$  is a strong electrolyte, then as each mole of  $\text{Ca}(\text{OH})_2$  yields 2 moles of  $\text{OH}^-(\text{aq})$ ,

$$\begin{aligned} [\text{OH}^-(\text{aq})] &= 2 \times 0.020 \text{ mol l}^{-1} \\ &= 0.040 \text{ mol l}^{-1} \end{aligned}$$

To calculate the pH,  $[\text{H}^+(\text{aq})]$  must be calculated from the ion product of water, at  $25^\circ\text{C}$ :

$$K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1.0 \times 10^{-14} \text{ mol}^2 \text{l}^{-2}$$

$$[\text{H}^+(\text{aq})] = \frac{10^{-14}}{0.040} \text{ mol l}^{-1} = 2.5 \times 10^{-13} \text{ mol l}^{-1}$$

$$\text{From the definition of pH} = -\log \left\{ \frac{[\text{H}^+(\text{aq})]}{\text{mol l}^{-1}} \right\}$$

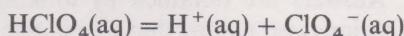
$$\begin{aligned} \text{pH} &= -\log (2.5 \times 10^{-13}) \\ &= -(\log 2.5 + \log (10^{-13})) \end{aligned}$$

Using your calculator,

$$\text{pH} = -(0.3979 - 13) \approx 12.6$$

As you should have anticipated, the solution is strongly basic.

**SAQ 16** (i)  $\text{Cl}_2\text{O}_7 + \text{H}_2\text{O(l)} = 2\text{HClO}_4(\text{aq})$



(ii)  $\text{HClO}$  (hypochlorous acid) is the weaker of the two acids:



You may be interested to know that for  $\text{HClO}$ ,  $K_a$  is only  $2.9 \times 10^{-8} \text{ mol l}^{-1}$  (Table 3).

You were told that one of the acids is strong and the other is weak. But from Section 6.3 we know that the higher oxide is the more acidic. Thus  $\text{Cl}_2\text{O}_7$  must form the strong acid and  $\text{Cl}_2\text{O}$  the weak one. Note however that both oxides are acidic, as are most oxides of non-metals (Section 6.3).

**SAQ 17** (i)  $K_a = 1.78 \times 10^{-5} \text{ mol l}^{-1}$ ; (ii) the ratio of un-ionized to ionized acetic acid molecules is 56.2.

(i) In the solution,  $\text{pH} = 3.00$ , so

$$\log \left\{ \frac{[\text{H}^+(\text{aq})]}{\text{mol l}^{-1}} \right\} = -3.00$$

$$[\text{H}^+(\text{aq})] = 10^{-3} \text{ mol l}^{-1}$$

As every  $\text{HAc(aq)}$  yields one  $\text{H}^+(\text{aq})$  and one  $\text{Ac}^-(\text{aq})$ :

$$[\text{H}^+(\text{aq})] = [\text{Ac}^-(\text{aq})] = 10^{-3} \text{ mol l}^{-1}$$

Thus in every litre there is  $10^{-3}$  or 0.001 mole of ionized acid. As the total amount of acid in each litre is 0.0572 mole, each litre contains  $(0.0572 - 0.001)$  mole of un-ionized acid. So,

$$[\text{HAc(aq)}] = 0.0562 \text{ mol l}^{-1}$$

Now  $K_a$  can be evaluated:

$$\begin{aligned} K_a &= \frac{[\text{H}^+(\text{aq})][\text{Ac}^-(\text{aq})]}{[\text{HAc(aq)}]} \\ &= \frac{(0.001)^2 \text{ mol}^2 \text{l}^{-2}}{0.0562 \text{ mol l}^{-1}} = 1.78 \times 10^{-5} \text{ mol l}^{-1} \end{aligned}$$

This is very close to the value in Table 3.

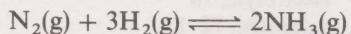
(ii) In each litre there are 0.0562 mole of un-ionized, and 0.001 mole of ionized acid. The ratio is therefore 56.2.

**SAQ 18** From Equation 50,

$$\begin{aligned} K &= \frac{[\text{HI(g)}]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} \\ &= \frac{(1.70)^2 \text{ mol}^2 \text{l}^{-2}}{(0.35 \text{ mol l}^{-1})(0.15 \text{ mol l}^{-1})} \approx 55 \end{aligned}$$

This is close to the quoted figure.

**SAQ 19** According to Equation 50, the equilibrium constant for the reaction



is given by

$$K = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3}$$

If  $\text{NH}_3(\text{g})$  is removed from the equilibrium system,  $[\text{NH}_3(\text{g})]$  is decreased, but at equilibrium, the right-

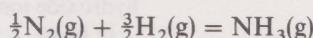
hand side of the above equation cannot fall below the equilibrium value. Consequently, the system responds in the way discussed in SAQ 8: more  $\text{N}_2$  and  $\text{H}_2$  react to form  $\text{NH}_3$  until the equilibrium value of the expression is restored. In this context, the predictions based on Le Chatelier's principle are just a direct consequence of the constancy of  $K$  at a given temperature.

**SAQ 20** (i) 0.944 mole of  $\text{NH}_3(\text{g})$ ; (ii) 0.475 mole of  $\text{N}_2(\text{g})$  and 1.426 moles of  $\text{H}_2(\text{g})$ .

At equilibrium,  $[\text{N}_2(\text{g})] = 0.0033 \text{ mol l}^{-1}$  and  $[\text{H}_2(\text{g})] = 0.0100 \text{ mol l}^{-1}$ , so

$$\begin{aligned} &\frac{[\text{NH}_3(\text{g})]^2}{(3.3 \times 10^{-3} \text{ mol l}^{-1})(1 \times 10^{-2} \text{ mol l}^{-1})^3} \\ &= 2.70 \times 10^8 \text{ mol}^{-2} \text{l}^2 \\ &[\text{NH}_3(\text{g})]^2 = 8.91 \times 10^{-1} \text{ mol}^2 \text{l}^{-2} \\ &[\text{NH}_3(\text{g})] = 0.944 \text{ mol l}^{-1} \end{aligned}$$

If we divide the formation equation by 2:



we see that every mole of ammonia is formed from  $\frac{1}{2}$  mole of  $\text{N}_2$  and  $1\frac{1}{2}$  moles of  $\text{H}_2$ . Thus the 0.944 mole of ammonia in the litre bulb was formed from 0.472 mole of  $\text{N}_2$  and 1.416 moles of  $\text{H}_2$ . If these amounts are added to the 0.0033 mole of  $\text{N}_2$  and 0.01 mole of  $\text{H}_2$  present at equilibrium, the total amount pumped in must have been 0.475 mole of  $\text{N}_2$  and 1.426 moles of  $\text{H}_2$ .

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